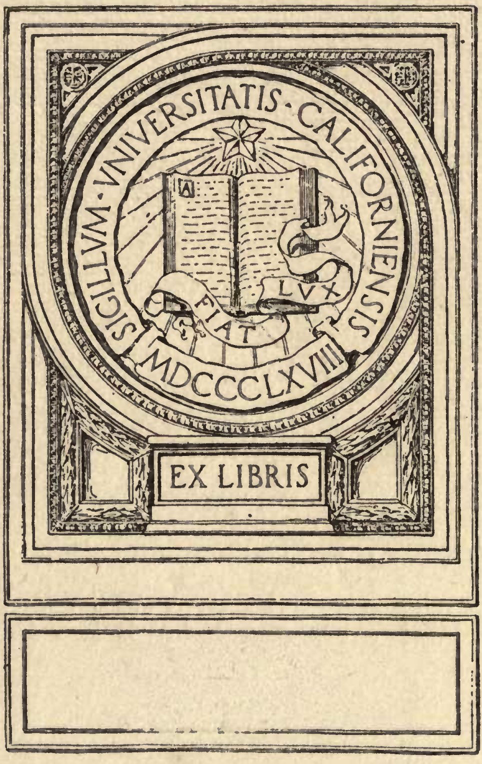
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1918.

PREFACE TO THE ENGLISH EDITION.

PRIOR to the outbreak of war Messrs. Griffin had secured the English copyright in this important book, and had arranged for its translation. The work of Messrs. Dubosc and Luttringer was evidently of permanent value, and supplemented such standard treatises as *The Chemistry of India Rubber*, by Dr. C. O. Weber, and *The Manufacture of Rubber Goods*, by A. Heil and W. Esch, already established in their Technological Series. Unfortunately, the translation has had to take second place to other pressing duties connected with the War, and has only been accomplished by utilising spare moments, but little, if anything, has been lost by this delay, as research in the direction of the authors' work has also necessarily been impeded.

To all interested in the cultivation of rubber, its modern chemistry and the preparation of synthetic rubber, this work must prove of great value, as a glance through the authors' preface and the Table of Contents will abundantly show. The Translator has corrected the many textual errors of the original, and Indexes have been added to facilitate reference.

E. W. L.

LOUGHTON, 1917.

AUTHORS' PREFACE.

To emphasise the great interest which attaches at the present time to all questions relating to rubber is unnecessary. During recent years this raw material has taken a position of very considerable and increasing importance in the industrial life of the world, as will be at once evident upon consideration of the somewhat dry statistics which we shall have occasion to quote.

One result of the tremendous rise in price which occurred in 1910 as the result of attempts to control the market for this product, has been to establish, as matters of every-day concern, the study of planting problems, and researches on the synthesis of rubber.

We thought that it would be of interest to collect into a single volume the scattered accounts of the work and views of various writers on the subject which have been published in a number of journals, some of which are not easy to procure, adding to these our own observations. We have sought in these pages to refer, as far as possible, to everything relating either to the cultivation or to the modern chemistry of rubber.

The first section of the book deals with natural rubber, attention being especially devoted to the study of plantation rubber, the appearance of which on the market has had unexpected results. The large amount of capital invested in the various exploiting companies, and the great number of the latter, are sufficient in themselves to justify the prominence we have given to this first section, were it only to correct, by means of the statistical information and costs of production repeatedly given, ideas—often absurdly incorrect—which are daily echoed by the financial reviews.

In this section we have also found a place, in keeping with their daily increasing importance, for the resinous rubbers, and for reclaimed rubber.

The second section deals with the formation, the properties, the analysis, and the constitution of natural rubber. This *résumé* of the modern chemistry of rubber forms a natural transition step towards the section dealing with its syntheses. In it questions of vegetable biochemistry relating to the formation of rubber in the plant have been entered into to some extent, and we have given particular attention to that unique phenomenon, coagulation.

Whereas we have given full accounts of the researches of Weber, Harries, Ditmar, Victor Henri, Bertrand, and Spence, we have not considered it worth while to recapitulate the earlier work on the properties and analysis of rubber. For this the reader is referred to such excellent works as that of Seeligmann, Lamy-Torrilhon, and Falconnet, in which full particulars will be found.

The last section of the book deals with the synthetic production of rubber.

Many investigators have rushed to the attack of this extremely difficult problem, and a great number of patents have been taken out.

We have sought to collect together, without bias, the various processes which have been published up till recently, and have made an effort to classify them according to the most rational scheme possible.

These synthetic methods are of very unequal merit, and without any wish to be stinting in approval, some of them can be justly termed far-fetched. There are others, on the contrary, of which the merit is so much the greater in virtue of the fact that they introduce new methods of general value in synthetic chemistry.

Despite our most careful efforts to include everything which appeared to be of any interest in connection with this synthesis, we are quite conscious of the fact that, as the subject is being constantly followed up, this section will need to be brought into line with later discoveries.

In a sense it is, indeed, the bitter fate of all scientific treatises to be born old. Nevertheless, if this contribution to the bibliography of rubber, with all its gaps and imperfections, should succeed in interesting economists, or in rendering any service to companion workers, we shall have been more than recompensed for the effort we have put into it.

A. D.
A. L.

Paris, 1913.

ERRATA.

Page 2, line 29, delete "Mexico."
Page 4, line 2 from bottom, for Herson, read Iterson.
Page 96, line 7, for Merellet, read Morellet.

CONTENTS.

THE SYNTHESIS OF CAOUTCHOUC.

SECTION I.

NATURAL RUBBER:

ITS PRODUCTION, ITS PRESENT POSITION, ITS COST OF PRODUCTION.

CHAPTER I.

INTRODUCTORY.

The indispensability of india-rubber to the every-day life of our present civilisation is too obvious to need urging. Its manifold applications have called into being a number of special branches of industry, which have, within recent years, undergone remarkable development under the stimulation of the continually increasing requirements of the consumer.

Fears might well arise that in the near future the supply will not be equal to the demand. In 1897, for instance, the consumption of raw rubber was only 7,000 tons; in 1910 it has increased to 70,000 tons, and a year later to 85,000 tons.

These figures represent an increase over the whole period, 1897-1911, at the rate of 5·5 per cent. per annum, and, assuming that the same rate of increase will hold good in the future, we may reckon upon a consumption of something like 130,000 tons in the year 1920. But seeing that new uses are constantly being found for rubber, it would seem reasonable to suppose that the rate of increase in consumption will be somewhat greater, say 6 per cent.; at this rate a conservative estimate of the requirements of the various branches of the industry in the year mentioned would be 140,000 tons.

If prices remain normal—that is to say, if fine, hard Para, taken as the standard of value, does not again rise to twelve or thirteen shillings per pound, the business done in the commodity will represent the considerable sum of £80,000,000 per annum, against Sir Henry Blake's estimate—in July, 1911—of £45,000,000. Dr. Karl Duisberg was, therefore, not far wrong when, in his lecture at the Munich Museum on October 5th, 1911, he estimated that the rubber industry is already twice as important as the colour industry, which represents an annual value of only £24,000,000. In making this comparison Duisberg referred to the great interest attaching to the problem of the synthetic production of a substance similar to rubber, but, in doing so, he laid stress upon the fact that, with wild rubber costing about 2s. 4d. per lb. to produce, and plantation cultivated rubber only 1s. 4d. per lb., the cost of the synthetic product must not exceed 10d. per lb. Such a low cost of production would only be possible if, as in the case of the colour industry, the starting point were a very cheap and abundant raw material.

The question arises, Will the supply of raw rubber be sufficient to meet the enormous and increasing demand?

Since the problem of the synthetic production of rubber has been solved, it can be said that there is no serious danger of a deficiency in the supply. Furthermore, in common with that of all synthetic products, the cost of production of rubber is certain to undergo a progressive reduction, and it may be anticipated with some confidence that, in a comparatively short time, the market price of raw rubber will revert to the level at which it stood before the wide expansion of the industry began to create a scarcity—and that in spite of a tenfold increase in the supply. The first result of the struggle between natural and synthetic rubber, which must inevitably take place before long, will be a reduction in cost, and the condition of affairs which obtains in the case of alizarin, indigo, and camphor is certain to be reproduced.

In order to arrive at sound conclusions in respect to this question, it is well to have all possible data at hand, and, therefore, before entering into the details of the synthesis of rubber, we propose to take a rapid survey of the present position of natural rubber. We shall endeavour, more especially, to form some estimate of the extent to which production is capable of expansion. Many attempts have been made in recent years to bring about an increase, either by forcing the yield from wild rubber-bearing plants, or by laying down plantations of carefully selected trees, in districts chosen with equal care; or, again, by making use of highly resinous rubbers, such as Jelutong, after they have been purified by removing the excessive amount of resins which they contain; or, lastly, by the "recovery" of old rubber. We shall also endeavour to ascertain the cost of production of rubber derived from each of the above sources.

Rubber-Producing Regions.—The three principal groups into which rubber-producing countries may be divided—America, Africa, and Asiatic-Oceania—are included within a belt of the earth's surface, about 800 kilometres (500 miles) wide, extending from latitude 30° N. to 30° S.

The countries forming the South American group are Brazil, Bolivia, Paraguay, Peru, Ecuador, Colombia, Venezuela, Mexico, and the Guianas.

The rubber collected in the Amazon basin is exported from Iquitos (Peru), Manaos (Brazil), and Belem. Other Atlantic ports from which it is shipped are Pernambuco, Parnahyba, Sao Luis de Mananhao, Fortaleza, Ceara, Bahia, Rio de Janeiro, and, in Uruguay, Montevideo, for the products of Matto Grosso, North Paraguay, and some from Bolivia. On the Pacific coast the ports of Arica in Chile, Mollendo in Peru, and Guayaquil in Ecuador ship rubber obtained from the western slopes of the Andes. There are also a few ports on the Caribbean Sea, amongst others Cartagena and Savanilla in Colombia, and Puerto Cabello in Venezuela.

The rubber-producing countries of Central America are Mexico, Guatemala, San-Salvador, Nicaragua, Costa Rica, and the Antilles, and the usual ports are Vera Cruz in Mexico, and Bluefields and Greytown in Nicaragua.

In West Africa rubber is produced in the following countries:—Senegal, Gambia, Portuguese and French Guinea, the Soudan, Sierra Leone, Liberia, the Ivory Coast, Gold Coast, Togo, Dahomey, Lagos, Nigeria, the Cameroons, Spanish Guinea, Gabun, the French and Belgian Congos, and Angola. The principal ports for the products of these countries are Kayes, on the Senegal, Rufisque, Bissao, Boulam, Conakry, Grand Bassam, Cape-Coast Castle, Accra, Lagos, Old Calabar, Libreville, Loango, Bruzzaville, Boma, Loanda, and Benguela.

On the East Coast of Africa the centres of production are Abyssinia, East Africa, Mozambique, Madagascar, the Comoro Islands, Zanzibar, Mauritius, and Réunion. The rubber from these centres is exported from Mombasa, Quilimane, Beira, Lorenzo Marques, Zanzibar, Nossi-Bé, Diego-Suarez, and Tamatave.

In Asia the principal places concerned in rubber production are British India, Burmah, Ceylon, the Malay Peninsula, Siam, Cambodia, Cochin China, Annam, Tonkin, and Laos.

In Oceania rubber is collected in one part of Australia, the Malay Archipelago, notably Sumatra, in Java, Borneo, New Guinea, the Philippines, New Caledonia, and Fiji.

The ports for Ceylon, Burmah, and Annam are Rangoon and Calcutta; for the Malay Peninsula and Malaysia they are Penang and Singapore, and, commercially, the source of the rubber is the Straits Settlements; whilst Java exports rubber from the port of Java, and French Indo-China from Hanoi.

In the midst of this vast assemblage of producing centres Brazil occupies a very prominent position; 38,000 tons of the raw material were exported in 1910—that is to say, nearly half the world's consumption.

Rubber-Yielding Plants.—The number of plants which yield a latex from which rubber can be obtained by a process of coagulation is very great; more than two hundred species of such plants have been identified. Most of these belong to four natural orders—viz., *Euphorbiaceæ*, *Artocarpeæ*, *Apocynaceæ*, and *Asclepiadeæ*; the rest, with few exceptions, to the *Moraceæ* or the *Sapotaceæ*. They are of very varied form and size; some are herbaceous, and contain the latex in their roots or underground stems; others are vines or climbers, which sometimes run to great lengths, and which yield latex from their branches; others again are shrubs. The greater part of the rubber which comes into commerce, however, is obtained from forest trees of more or less considerable size.

South America, and more particularly Brazil, which may be said to be the rubber-producing country *par excellence*, is the natural habitat of the genus *Hevea*, the most important of the *Euphorbiaceæ*. The trees of this genus grow to a height of from 50 to 65 feet, and attain a diameter at the base of from 63 to 67 inches. The *Heveas* flourish in low-lying country, where the soil is moist and, at intervals, flooded: but there are also varieties which grow in drier situations.

In this vast region there are to be found many different species of *Hevea*, some of which are not at all well known as yet. On the lower Amazon the natives distinguish two kinds of *Seringas* (*Heveas*), naming them respectively the "black" and the "white"; the former is reputed to yield rubber of the higher quality, but, as a rule, the latices of the two kinds are mixed together before coagulation. On the upper reaches of the river, where it joins the Rio Negro, two other kinds of *Hevea*, yielding products which are not identical, have been reported—viz., the *Seringa torrada* and the *Seringa verdadeira*. In the basin of some of the tributaries of the Amazon, again, Coudreau has found very distinct *Heveas*, which grow on the slopes of the Andes, up to a height of 26,000 or 29,500 feet; these trees are very robust, but yield relatively small quantities of rubber. The *Seringa torrada* was the first species of rubber tree encountered by La Condamine, and from it were obtained the samples which he sent to the Academie des Sciences in 1737: the fruits of this particular species are smaller than those of the *Hevea* of the lower reaches. Contrary to frequent statements, the latter species is not

Hevea braziliensis—the habitat of which is the region of the upper Orinoco—but *Hevea Siberi*.

Another rubber plant indigenous to this part of the world, the *Manihot Glaziovii*, which has recently been exploited to a much greater extent than formerly, is a tree which flourishes more particularly in the infertile, dry, and stony districts of the province of Ceara, and of the States of Piauhy and Marañao. Cross, who has made a special study of the tree, says that it is noteworthy in particular because of its unconventionality. It delights in stony districts, in spite of the dryness, amounting to aridity, of the soil. At a casual glance it resembles a birch tree, and has a crown of leafy branches in the form of a basket with its sides bent over towards the ground. The bark peels off naturally in silver-grey shavings: the roots are covered with excrescences, which are sometimes as large as a potato. When the tree is young these excrescences are soft and spongy, and contain a certain amount of latex, which, however, disappears as the tree develops. Judging from this very condensed information, it would be of great interest to make a closer study of the *Manihot*, for it is very probable that an insight into the mechanism of the formation of latex in the plant could thus be gained. The process seems to be, according to Cross, very like that involved in the formation of starch in the potato.

Of the *Euphorbiaceæ* one other genus is deserving of mention. The *Sapium* thrives both in the moist plains and in mountainous regions, for it has been found growing on the slopes of Chimborazo. The rubber obtained from it is of a very high quality, and is known as *Caucho blanc* (white caucho). Of the *Artocarpeæ* the chief representatives are the *Castilloa*, a tree which frequently grows to a height of 130 feet, with a girth of 16 feet, found in Mexico and Peru; and the *Ficus elastica*, the *Artocarpus*, and the *Cecropia* in Indo-China, the Dutch Indies, and Borneo.

The natural order *Apocynaceæ* includes both trees and creepers. Amongst the former are the *Hancornia* or *Mangabeira*, found in Central Brazil; the *Funtumia elastica*, in the Ivory Coast and Cameroons; and the *Mascarenhasia* in Madagascar. Of the creepers, or lianas, most of which belong to the genera *Landolphia* or *Gohina*, and are indigenous to Africa, growing in the Congo, the Soudan, Mozambique, and Madagascar, the most important are the *Carpodinus*, the *Leuconotis*, the *Willoughbeia*, the *Kickxia*, the *Urceola*, the *Parameria*, and the *Forsteriana*. The *Asclepiadeæ* are plants with herbaceous branches, and include the African genera, *Callotropis*, *Cynanchum*, and *Cryptostegia;* and the *Djera Costulata* and *Alstonia* of Sarawak, from which the so-called Gutta Jelutong is obtained. In addition to all these there remains to be mentioned the *Parthenium argentatum*, the source of *Guayule rubber*, a product which occupies a class by itself, with respect both to its method of production (mechanical separation from the tissues of the harvested shrub), and to its properties.

Output of Rubber from the Various Regions.—Having surveyed the geographical sources of rubber, we may now pass on to ascertain the possibilities of the yield of rubber from each of the regions in question, and to consider what defence can be put up by the natural product against the assault which will be made upon it in the future by synthetic rubber.

America.—Amazonia,[1] the chief of the collecting districts, has an area

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[1] For an account of the cultivation and collection of rubber, see Henry C. Pearson, *The Rubber Country of the Amazon.*

of 2½ million square miles, about twelve times that of France. Throughout this immense region, as La Condamine showed as early as 1745, one or other of the numerous varieties of *Hevea* or *Castilloa* is to be found, but most frequently *Hevea braziliensis*, that wonderful tree, which, when carefully tapped, will yield in its maturity at thirty-five years of age as much as 22 lbs. of rubber per annum.

It is estimated that there are 200 million trees in the two States of Para and Amazonas, and that 50 per cent. of these are being tapped. In Amazonas the field of exploitation of the natural seringals is daily increased by means of exploration carried right up into the most remote ramifications of the great rivers which flow into the Amazon. Unfortunately the very primitive methods employed in working the *estradas*, together with the well-nigh impossible means of transport, render the price obtained for the product very unremunerative, especially when the exorbitant export duty—22 per cent. *ad valorem*—which is put on when the rubber leaves Brazil, is taken into account.

In the State of Para, where it is easier to work the trees, and especially in the Delta, and on the islands at the mouth of the Amazon, the yields, although still considerable, are decreasing rapidly as the trees become exhausted by repeated tapping—often badly carried out. In 1903 a case was cited by Plan of a seringal in Rio Madeira which, after 40 years' working was only yielding 500 lbs. per man per annum, one-fourth of its normal output. M. Lecointe, in the course of a series of extremely interesting articles in *Le Caoutchouc et la Guttapercha*, from which we shall have frequent occasion to quote, says that to-day the whole of the seringals of Lower Madeira, and of the islands, are in the same condition; in spite of the advantages of proximity to a port, good methods of collection, and the high quality of their products, it is becoming increasingly difficult to make the industry pay.

Amazonia would thus appear to have reached the zenith of its rubber-producing power; the increase of, possibly, some thousands of tons, which will no doubt result from further exploitation of the more remote regions, will be counterbalanced by a decrease due to exhaustion of the older seringals. The only thing which could possibly increase production in this part of the world would be the creation of a plantation industry in the vast *varzeas*—uncultivated tracts of country on the banks of the Amazon, which are peculiarly adapted to the cultivation of *Hevea*. Nothing, or practically nothing, has been done in this direction up to the present, and it must be remembered that a rubber plantation hardly counts until it is ten years old.

The best Brazilian rubber is obtained from *Hevea braziliensis*. In the collection of this rubber the *patrãos* act as middle men, and receive cash advances from the rubber-exporting firms of Para and Manaos, often amounting to several hundred thousand francs. These *patrãos* employ the *seringueiros*, of whom there are two classes, *seringueiros* proper, who work the genuine *Hevea*, and *caucheros*, whose operations are devoted to an allied species, which yields *Caucho* rubber.

The work of these operatives begins in the early morning, because the trees, freshened by the night dews, yield much more latex then than during the rest of the day. The first incisions are made in the tree with a small iron hatchet-like instrument, called a *machatinhe*, or with Van der Kerkhove's "incisor," at a height of about 2 metres from the ground. The latex begins to flow at once, and is collected in little tin-plate cups, called *tigelinhas*, fixed at short distances apart on the tree.

On the following day incisions are made a little lower (25 cm.) down, and the positions of the cups are altered accordingly, and so on until at the end of a week the incisions are made close to the ground. The lower down the incisions are made the greater is the flow of latex. A whole series of trees is treated in this fashion during a week, and at the end the latex is collected by a child. An *estrada*, or group of trees, which can be dealt with in this space of time, yields on an average 1½ to 2 gallons of latex, equivalent to 9 or 10 lbs. of rubber, per day.

The process of coagulation, which the *seringueiro* proceeds to carry out when the whole of the yield of an *estrada* has been collected together, remains the same, practically, as described by La Condamine and by Fresneau, a hundred and fifty years ago.

The latex is freed from such impurities as earth, bark, and leaves by a rough filtration into a tin-plate vessel. A fire, fed with the nuts of the palm tree, *Attalea excelsa*, together with green, resinous wood, is then lighted, and the dense smoke from it is localised by leading it up through an earthenware chimney. Two forked poles are fixed in the ground, one on either side of the fire, to serve as supports in which a large wooden *forma* or paddle, with a long handle at one end, and pointed at the other, can be slowly rotated by the hand of the operator. The latex is allowed to flow in a thin stream, through a cock with a flattened spout, on to the broad part of the paddle, while the latter is slowly revolved in the smoke from the fire. The latex coagulates at once, and a further quantity is allowed to flow on to the paddle, where it covers the first layer and is in turn coagulated This process is repeated until a mass of rubber, weighing from 20 lbs. to a cwt.—according to the locality—has been built up on the paddle. The rubber thus prepared, which generally has the initials of the owner cut on it, is called *borracha fina*, and constitutes the most expensive grade of "*fine Para.*"

On the Lower Amazon the manipulation has been simplified and rendered less arduous, and, in addition, the yield has been improved by the use of handier forms of smoking apparatus than the classic *boiao*, such as Van der Kerkhove's *fumero* or Danin's smoking machine.

The question of labour obviously plays a very important part in connection with the cost of production, and, as Lecointe[1] has shown, in Amazonia labour is both scarce and expensive. The mortality amongst *seringueiros* is terribly high, and is no doubt due mainly to the lack of proper food, and to the enfeebling effects of careless living. Such conditions render the men very liable to fevers and to diseases such as beri beri, which are endemic in these humid forest regions, where there is little opportunity for the sun's rays to purify the soil from the decomposing organic material with which it is covered. The half-nomad *seringueiro* does not become much attached to a locality which he has not had to cultivate in order to obtain his abundant harvest. Having left his native place and gone to the seringal at the call of some employer or other, attracted by the hope of speedy riches, his one object in life is to collect rubber and get back home again. He does no planting or sowing, and rears no live stock, and his commissariat has to suffer accordingly. He lives almost entirely on dried, salt meat, manufactured for him in Southern Brazil and the Argentine, and taking several months to reach him, and on beans and manioc flour sent to him from Maranao; moreover, he is fortunate if the boat which brings him this coarse food does

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[1] *Le Caoutchouc et la Guttapercha*, **1911**, 8, 5529.

not run aground on the way, or get sunk in collision with some tree trunk cunningly planted in the mud. Add to this the dangers to which he is exposed in the daily round of his *estrada*, during the months when the yield is best, from November to April, along the faint tracks through the forest, intersected by swamps and frequently flooded; and in his night work on the marshy ground, which must be done if he is to have all his collecting cups in position before daybreak. And after the collection of the latex comes the process—arduous and unhealthy—of smoking it, when, under some crude shelter, open to all the winds that blow, his face scorched by the heat of the palm-nut fire, his back exposed to the rain, half-suffocated, and with his eyes smarting with the smoke, his one concern is, as skilfully as may be, to distribute uniform layers of latex over the ball of rubber, which he turns over and over in the smoke of his fire.

It is scarcely to be wondered at that, after the stupefying effect of ten or fifteen days of this kind of life, he takes advantage of his next visit to his employer's *barracon* to bury his cares in drink, and becomes a ready victim of all who, from interested motives, are eager to put temptation in his way. The end of all this is that he succeeds in ruining his already enfeebled constitution.

One hundred and fifty thousand *seringueiros* are required to carry on the exploitation of the trees, and of these some 4,000 disappear every year; they are replaced either by natives from the States of Marañao, Piauhy, Ceara, and Rio Grande del Norte, or by casual labourers emigrating from France, Belgium, or Italy. The latter class form the better type of labourer, for the half-breed natives are by nature careless, and the laziness of the Amazonian *seringueiro* is proverbial.

Under these conditions it is estimated that the cost of collection of the rubber is about three times as great as in Ceylon and the Malay Peninsula.

Although a large producer, therefore, Brazil appears to be the country which is in the least favourable position to carry on a struggle against synthetic rubber, on account of the high cost of labour, the difficulty of transport, and the huge export duty payable to the State.

In the case of this country, where the production is great, and where the quality of the product is of the highest, the consideration of the relationship of cost price to selling price forms an interesting and, under existing circumstances, extremely important study.

The following *résumé* gives the price of first grade Para rubber from 1887, when the consumption of rubber began to show a serious increase, until 1911:—

PRICES OF FIRST-GRADE PARA, 1887-1911.

YEAR.	PER LB.	YEAR.	PER LB.
1887,	3s. 3d.	1900,	4s. 6d.
1888,	3s. 2d.	1901,	3s. 10d.
1889,	3s. 0d.	1902,	3s 6d.
1890,	3s. 8d.	1903,	4s. 4d.
1891,	3s. 3d.	1904,	5s. 0d.
1892,	2s. 11d.	1905,	5s. 9d.
1893,	3s. 2d.	1906,	5s. 6d.
1894,	3s. 2d.	1907,	4s. 6d.
1895,	3s. 4d.	1908,	4s. 2d.
1896,	3s. 6d.	1909,	7s. 5d.
1897,	3s. 8d.	1910,	9s. 11d.
1898,	4s. 2d.	1911,	5s. 6d.
1899,	4s. 5d.		

The average price for the whole period of 25 years was 4s. 5d. per lb.

Speaking generally, one may say that, apart from fluctuations brought about rather by irregularity of production than by variations in consumption, the value of rubber has increased continuously from the time when it began to be largely used industrially, and more especially in connection with locomotion.

Fifty years ago the higher grades of rubber were selling at from 2s. to 2s. 6d. per lb.; since that time the price has, therefore, been double, and at certain periods four times, what it was. The increase has been most marked since 1896, and has followed the popularisation of motor vehicles of all kinds. This continuous upward movement of price—the set-backs to which have been few and of short duration—has been due mainly to the ever-growing demand for rubber on the part of the expanding industries which make use of it. When one considers how extraordinarily rapid has been the recent development of some of these, for example the pneumatic tyre industry, it is easy to see how difficult it has been for production to keep pace with a consumption subject to such great annual increase.

If we were to be dependent on the two natural sources, the exploitation of wild rubber plants and the development of the plantations, to meet the demands of the industries, which show the reverse of any tendency to grow less, it would seem that an early drop in the price of raw rubber cannot be counted on.

The only thing that could, without further increase in price, supply all the demands of the increasing consumption would be the entry into the field of synthetic rubber. Such an eventuality would have, too, the beneficial effect of creating a steadier, more healthy market, and of preventing any future attempt at cornering for the purpose of establishing fictitious values, like those already seen in 1909 and 1910.

However great may have been the demand at that time, the prices of 7s. 6d. and 10s. per lb., which were obtained—even 12s. and 12s. 9d. were reached in London, Antwerp, and Hamburg—were not due to a deficiency of the raw material. Serious investigations made in the market go to prove that these abnormally high prices were the result, not of a shortage of the material, nor of an excessive demand, but of speculative operations.

As a matter of fact there was formed about 1910, in Para-Belem, the market to which almost all Brazilian rubber gravitates, a "valorisation" syndicate, with the Bank of Brazil at its back; the business of this was to maintain a high level of prices by cornering the product and only letting it go at prices fixed in advance. This league of *Aviadores* received the support of the Governments of Para and Amazonas, in the enactment of various measures which made it possible for them to secure the financial resources necessary in order to effect the cornering, and to force prices up to 14s. 6d. per lb. The very important arrival of plantation rubber on the market, combined with a decrease in the demand—manufacturers having been rendered nervous by the unjustifiable exactions of producers—brought about a reaction, and so far from rising the price of raw rubber fell to a normal level of 5s. 6d. per lb. in 1911. This combination, which was a brilliant success in the case of coffee, was much less so in the case we have just described, and the Federal Government of Brazil, which receives some 115 millions per annum in duties on the export of rubber from the rubber-bearing provinces, was obliged to intervene in order to prevent a catastrophe. A series of measures were passed, of which Marshal Hermes de Fonseca, the President of the Republic, was himself the inspiration, and which will take a certain number of years to bring into operation. The main points in these measures are the following :—

All utensils and materials for use in the cultivation, collection, or improvement of the three kinds of rubber trees (*Hevea, Mangabeira, Maniçoba*), whether intended purely for the extraction of latex, or for the cultivation of the trees, are to be exempt from all duties.

Bounties are to be given for those rubber enterprises in connection with which some supplementary cultivation has been carried out in such a way as to make good use of the land, and also for entirely new cultivation of any one of the three rubber trees.

Experiment stations and trial gardens are to be started in various provinces. The export duties, both Federal and State, are to be reduced by 50 per cent. in favour of all rubber from wild *Hevea;* they are to be done away with altogether in the case of rubber from plantation *Hevea.* Various measures for facilitating emigration, and for establishing hospitals and dispensaries, even in the remotest parts of the Amazon basin, round off these preliminary arrangements in a very happy manner.

In completion of this plan of reform contracts for two lines of railway were to be issued; one line to connect the Madeira-Mamoré railway with the Peruvian frontier, and the other to link up the Amazon valley with the North-Eastern and the Southern States; the reduction of freight by this means would be very considerable. If this plan is carried out, and the necessary financial resources found to ensure its success, it is obvious that the price of rubber will drop. But it is at least doubtful whether the fall will be in time and of sufficient extent, and the future of Brazilian rubber is, therefore, a somewhat uncertain one.

In Mexico, although there may have been some development in the cultivation of Castilloa, and in the collection of Guayule, and although the total production of rubber in 1911 reached nearly 14,000 tons, it does not seem that it will be very easy to increase the yield; or if the yield be increased it will be at the expense of the vitality of the trees, and will result in the production of a lower grade rubber. This, particularly in the case of Guayule, is a serious matter where the quality is already not appraised at a very high value. Besides, figures which have been put forward on this point are very much open to doubt; and if the statements of Juan Ludwig in *Der Tropenpflanzer* be referred to, the production for 1909 did not, in spite of official statements to the contrary, exceed 6,000 tons, of which 5,600 tons consisted of *Guayule* exported from Ciudad Porfirio-Diaz, Vera-Cruz, and Lorido, and 400 tons of *Castilloa* from Tampico. In 1910, according to the French Chamber of Commerce in Mexico, 8,000 tons of rubber were collected. *Guayule* constitutes, as will be noticed, the great bulk of the rubber exported, and as its production involves the destruction of the shrub which yields it, the question is raised as to how long it will take to re-grow the latter.

The production of other parts of South and Central America is quite small: Bolivia yields 1,000 tons from *Hevea* and *Caucho;* Venezuela, 250 tons; and San Salvador, Columbia, Nicaragua, and Costa Rica some 100 tons between them from *Castilloa costaricana.* These figures are derived from the investigations of Pittier, Cook, Collins, Harries, and Renson.

It is not very likely that these figures will increase, because *Castilloa,* which is the chief source concerned, can never, on account of its low yield—4 or 5 ozs. of rubber per annum—form the object of a paying enterprise.

The French, Dutch, and British Guianas have a more promising future before them: in round figures these three countries produce between them about 1,000 tons, of which Cayenne contributes only an extremely small percentage. Still, seeing that *Hevea guayanensis* is a tree which, according to Van Asbeck and Cramer, closely rivals the Brazilian trees in robustness, a better conducted exploitation might have great results. Unfortunately, although the forests of Cayenne are rich in trees, and are near the coast, little has been done with them; money, too, has been lacking to make the necessary roads, and to recruit the *seringueiros* who would have to be brought into the country. The infatuation exhibited by capitalists for the East Indies and their plantations has caused them to totally neglect those of the West, whatever might be the resources which they had to offer.

The total production of America may be estimated at the present time at about 49,000 tons, and, leaving Mexico out of account, it would seem to have reached its maximum.

Africa.—The production of Africa, inferior in regard both to quality and quantity as compared with that of America, amounts to about 20,000 tons per annum, and is made up as follows:—

AVERAGE YEARLY PRODUCTION OF AFRICA.

The Congo and Angola,	8,250 tons.
Belgian Congo,	3,750 ,,
E. Africa,	480 ,,
Gambia,	10 ,,
Gold Coast,	1,600 ,,
Nigeria,	700 ,,
Togoland,	500 ,,
Sierra Leone,	100 ,,
Uganda,	1,000 ,,
Ethiopia,	125 ,,
Senegal,	630 ,,
Guinea,	1,530 ,,
Ivory Coast,	1,400 ,,
Upper Senegal and Nigeria,	270 ,,
Madagascar,	750 ,,
Other Parts,	200 ,,

It is of great interest to consider the possibilities of bringing about an increase in the productive capacity of this part of the world, by making improvements in the methods by which its vegetable wealth is being exploited; but it is not an easy matter to arrive at definite conclusions, because, in the first place, one has to begin with inaccurate or insufficient data. Whereas in South and Central America rubber is obtained almost exclusively from trees like *Hevea*, *Castilloa*, and *Manihot*—*Guayule* is, of course, an exception—and the methods of collection, with a few reservations in regard to processes of coagulation, are practically the same in all cases, in Africa quite another state of affairs exists.

There the rubber-yielding plants are of various types; in some cases trees, like *Funtumia*, in others shrubs, creepers (lianas), or plants with rhizomes, without counting the various new species which are constantly being discovered by explorers in a country of which the interior is little known, especially from the botanical point of view.

Each of these species of plant obviously demands a special method of treatment, and if the object be to conduct their exploitation in such a way as, whilst having an eye to the future, to obtain the most profitable present yield both as regards quantity and quality, it must be confessed that the mode of procedure has been badly thought out and established. In collecting rubber from herbaceous plants, the usual method of procedure is the following:—The roots of the plant are dried in the sun and are then cut up into small pieces about 12″ to 15″ long; these fragments are then placed on a tree trunk, and the bark is removed from them by beating them with a mallet. The pieces of bark are then treated in the same manner, and the latex which is thus forced out of the tissues dries up quickly, forming masses of rubber. This is cut up into pieces and purified by being put into several changes of boiling water, after which it is massed in sheets about half an inch thick.

In the case of the lianas, the following crude method has been employed right up to recent years:—The stems were cut up into pieces about a yard long, and piled into regular heaps about a central fire of logs; the latex exuded from the cut ends, and was collected in a hole dug in the ground at the foot of each heap. There is nothing rational about such a method of collection, but, as has already been said, it must be recognised that the establishment of a rational method is not an easy task. The question is an exceedingly complex one, for in Africa we have to deal, not with a single type of rubber-yielding plant, but with numerous species; even if the exploitation of them all were found to be possible, both from the point of view of quality of the product and financially, it is at least doubtful whether products of these types would answer the requirements of users who have been made difficult to please by the excellence of the American type.

The investigations of many French, English, German, Portuguese, and Belgian travellers have brought to light the existence of various kinds of rubber-yielding plants in tropical Africa. There are lianas of different degrees of development, yielding rubber from their branches or from underground stems; herbaceous plants, only the underground portions of which are rich in rubber; and trees with trunks which can be tapped. Some curious details respecting the lianas and plants with laticiferous tubercles are given by Geraldes and Fragateiro,[1] by Ferréne,[2] and above all, by Wildemann, the learned curator of the Botanic Gardens in Brussels, whose very striking articles we shall have frequent occasion to quote.

"Amongst these three great groups of plants," he says,[3] "one comes across good rubber producers, which have been exploited by the negro either for a long time, or since we have been trying to colonise the different regions of Africa, and to develop their natural riches."

Let us suppose for a moment that it may be possible to select from each group of rubber-yielding plants only one type which gives a large yield; it is not likely that it would be found possible to cultivate this type in the various regions of Africa, for once out of its normal environment the conditions demanded by its nature would be missing, and progress would be barred. But side by side with this question of replanting, if, as the result whether of rational exploitation or of barbarous methods of collection, the forests began to get exhausted, there is another factor of first importance,

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[1] *Le Caoutchouc dans les Colonies Portugaises,* Lisbon, 1910.

[2] *Le Funtumia Elastica,* Paris, 1910.

[3] *Caoutchouc et Guttapercha,* 1911, 8, 5028.

as in America—namely, the labour question. We have already explained the niceties and the troublesome side of this question as it exists in America, but in Africa the type of labour is decidedly inferior. The Brazilian *seringueiro*, in spite of his roughness, the Javanese coolie, and the native of Ceylon are undoubtedly of much sharper intelligence, and much more energetic than, with rare exceptions, the African native.

Lecointe's work on Brazil and Cramer's report[1] on Malaysia both emphasise the great care which must be bestowed upon the trees which are to be tapped. Can the African negro, indisposed to work regularly, idle, careless, be induced to give such close attention to his work? It is hardly probable, and even if it were it is almost certain that he could not be taught to carry out properly the delicate operation of smoke-curing, in virtue of which Para holds its position of superiority. This is clear from the fact that even on plantations directed by Europeans, and on which all operations are carried out with the greatest care, it has not yet been found possible to apply this method of coagulation perfectly: possibly better results may be obtained by means of the process recently proposed by Pahl in which the atomised latex[2] is brought into contact with carbon dioxide.

On the other hand, whereas the work of Weber, to which fuller reference will be made in a later chapter, has led to a fairly accurate knowledge of the exact composition of fresh American latex, and to the discovery of the function of the albuminoids and oxidases present in it, such knowledge is not yet at hand in the case of the greater number of African latices. We have indeed become familiar with the nature of the latices collected in Madagascar, through the interesting investigations of Jumelle and Perrier de La Bathie, and it is possible, as a result of their work, to devise rational methods of treatment, but this is far from being the case with the latices of the tropical zone, and especially those of the Congo.

If, on the one hand, it is possible to recommend the exploitation of trees by the method of tapping, what method, on the other hand, can one advise for the collection of the latex from lianas and herbaceous plants? Must the natives be allowed to continue to employ the brutal process, which consists simply in the chopping down of the plants?

There has been much hostility towards this mode of operation, which, in the opinion of some, will lead to a rapid exhaustion of the reserve supplies; a number of the colonial governments have taken the matter in hand, and have issued numerous regulations to try and put a stop to it.

The decree of March 25th, 1910, of the "Gouvernement Général du Congo Belge," for example, says:—"The latex of rubber trees must only be collected by making incisions or cutting grooves in the bark of the tree-trunk, without penetrating into the cambium. Latex must only be collected from lianas by means of incisions or grooves, or by cutting down the plant. Pulling up, incising, and cutting up the roots of the plant, as well as incising, grooving, and cutting up the main stem to a height of 1½ metres from the ground are prohibited."

The Government of French West Africa has gone further still; by a decree dated April 5th, 1911, it has forbidden in Upper Senegal, and on the Niger, all tapping between the months of July and October; has prohibited all movement of rubber in the country without a permit, and has insisted on

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[1] *Der Cultur von Hevea, Handleiding den Planters,* VOL. I, Amsterdam, 1910.

[2] *The Rubber Industry,* London, 1911, p. 234

all rubber passing the Control Office at Kayes, on its way to Dakar and Saint Louis. In this way it is hoped to preserve the *Gohina* lianas, which still exist in the Soudan. The destruction of rubber trees in Zanzibar, the exhaustion of the forests of Shamba Hill, from which the *Mascarenhasia* has almost entirely disappeared, the de-afforestation of Madagascar, are examples which afford some justification for such administrative measures. Jumelle and La Bathie tell us[1] that in Madagascar rubber plants have succumbed to the treatment of the natives, who, not content with scoring the trunk of the tree without any method, chop off all the tubercles, and the very roots on which the tree depends for its power of resistance. As soon as a tree reaches the rubber-yielding age it is " bled white," and dies within the year. It is thus easy to understand why there are no mature *Intisys* in the island, and since it is on these that its propagation by means of seed depends, the species is doomed to extinction. Portuguese East Africa has been ravaged by similar methods, and a like evil fortune has befallen Nossi-Bé, Sainte Marie, and all the islands in the neighbourhood of Madagascar.

" One of the most controversial subjects in connection with the exploitation of rubber trees," says Wildemann, " is that of the extraction of the latex in order to obtain rubber. Three hypotheses as to the function of the latex, all of which have much to be said for them, have to be considered. According to one this liquid, which contains a number of different substances, is looked upon as a waste or excretionary product of the plant; another regards it as serving the purposes of defence against the tree's enemies; whilst a third maintains that at any rate certain of its constituents are utilised by the plant in its life activity (or nutrition). In any case, it is probable that the removal of latex always produces some disturbance in the life of the rubber tree. It follows that to tap a tree is to diminish its vitality, and consequently to lessen its power of resistance to disease." The exhaustion of the districts of the Lower Amazon, already referred to, has this for its sole cause, and experiments carried out on plantations in Ceylon and Java have demonstrated that the frequency and malignity of the diseases to which the plant is subject increase with the extent to which it is worked.

In the tapping process, with frequent rest intervals, the whole of the bark of the tree trunk is removed at the end of a certain period, and must be gradually reformed by the tree; there comes a time, therefore, when not a fragment of the original bark remains on the tree, then tapping is begun again on a bark which is often not more than four years old; clearly the tree cannot successfully resist such a stripping, and it cannot be tapped indefinitely. Wickham, the creator of the plantation industry in Ceylon, who speaks with undeniable authority on this subject, has protested vigorously against such methods[2]; to this lingering death he prefers the crude methods of the natives, and recommends, for places like Africa, felling in place of tapping, with freedom to replant.

But the objection may be raised that by the application of this barbarous method the producing plants will be surely destroyed, and the country's resources annihilated. In the opinion of Wildemann, however, such a conclusion is open to discussion. If it be left to the native to cut down indiscriminately all the rubber-yielding plants he may come across, the result will no

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[1] *Caoutchouc et Guttapercha*, 1911, 8, 5343.

[2] *On the Plantation, Cultivation, and Curing of Para Indiarubber*, London, 1908, p. 37, etc.

doubt be a shrinkage in the sources of production; this has actually occurred in West Africa and in Madagascar, and in such circumstances the intervention of the local governments is highly justifiable. But if care be taken to select the plants which are to be cut down, even granting the native permission to carry this out whilst offering him no incentive to over-production, the stumps of the plants, especially the lianas, will throw up new growths capable of yielding rubber, always provided that the roots are not injured. As a matter of fact, it is the system employed in the French forests, known as the system of exploitation *par cantonnement*, or by marked trees, similar to that employed so judiciously by the Japanese in Formosa in the case of camphor, which should be adopted in tropical Africa. Although Brénier[1] is opposed to such a method, it is supported by Wildemann, Henri, and Chevalier.

Chevalier was extremely clear on this subject in his report on returning from his mission to French West Africa. He says: "It is necessary not only that the lianas and herbaceous plants should be dealt with by the method of cutting down, but that a similar, carefully controlled method should be adopted in the case of the trees like *Funtumia*, and not merely with the object of obtaining a maximum yield, but also to make sure of maintaining and even increasing the size of the plantations; for in the case of *Funtumia*, for example, the new growths combined with re-stocking will ensure the permanence of the undertaking.

The three types of African rubber-yielding plants—herbaceous plants, lianas, and *Funtumia*—will all yield, under suitable mechanical treatment, the rubber which is contained in their tissues, but which is not to be extracted by tapping processes. It is our opinion that, under present circumstances, the felling method is to be preferred, at any rate in tropical Africa."

Under these circumstances, and until "*cantonnement*" and re-stocking are realised, either by the laying out of copses, and nurseries for seeds and cuttings, or by means of plantations, one may regard the African forests—little known as they are, and where means of surveillance are lacking—as having reached their zenith as regards the production of marketable rubber, and that in future years exports from these regions will continuously decline.

Asia and Oceania.—In Asia and Oceania the rubber question presents itself under quite another aspect from that in America and Africa. Apart from those yielding the highly resinous rubbers, of which immense numbers are to be found in Malaysia, Borneo, and all the Dutch Indies, rubber trees may be said not to exist, in a state of nature, in these two quarters of the globe. Yet, judging from the character of the soils and the climate, this would appear to be the region in which planting—introduced by Wickham in 1876—ought to succeed best, and to promise interesting results.[2] Whilst in other parts of the world the efforts made to acclimatise *Hevea* have been almost in vain, very fine yields have been obtained from this somewhat delicate plant in Asia and Oceania.

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[1] *Le Caoutchouc d'exploitation, son avenir*, Paris, 1910.

[2] The earliest experiments in planting rubber date back a long way. According to Dr. Axel Preier (*Tropenpflanzer*, 1900), the first plantation was formed at Subang, in the Province of Tjiasem, in 1864-1865, and comprised about 100 acres, planted with 5000 *Ficus elastica* trees. Tapping was not begun until the trees were 18 years old, when they were found to yield 20-25 ozs. per tree.

Plantations.—After methodically conducted trials, extensive plantations were laid down by the British, in 1876, in Ceylon and the Federated Malay States; by the Dutch, in 1882, in Java, Sumatra, and Borneo; and by the French, in 1885, in Tonkin, Cambodia, and Laos.

The *Hevea* was chosen for these experiments as yielding the rubber reputed to be of the highest quality; difficulties were encountered; *Hevea* seeds rapidly lose their germinating power, and it was found necessary, in order to transport them, to plant them in soil and allow them to germinate on the voyage. The varieties of *Hevea* which have been selected do not demand for their culture a district which is periodically flooded like the Amazon basin, although they need a warm and moist climate. It is for this reason that French Tonkin has proved to be quite a wonderful country for the cultivation of rubber. Propagation is effected by seeds, where possible, but more often by cuttings planted 8″ by 8″, or 12″ by 12″ apart. The young plants are planted out into fields of 10 to 15 acres, bordered by roads from 10′ to 16′ wide; a distance of from 10′ to 12′ is allowed between the trees, which are planted in quincunx. As the trees grow they are thinned out so as to double the distance between them.

As these plantations are usually formed on the sites of forest clearings, it is customary to leave a few shelter trees standing during the early years.

Hevea begins to yield rubber in workable quantity when 6 to 10 years old. At first the trees are only tapped every other year; later on, when they mature, they can be tapped every year. The operation is carried out after the rainy season, and never during the period of flowering. At the start the tree yields a little over a pound of rubber per annum, but the yield increases as the trees grow older, and may reach as much as 3½ to 4½ lbs.

Attempts have also been made to cultivate *Manihot Glaziovii* and *Castilloa; Manihot* in particular lends itself to an easy method of cultivation, and will flourish even in poor soils in arid districts. This species is propagated by seeds, the hard integument of which must first be split or filed. The tree grows rapidly, if care be taken at first to shelter it from the wind, and it can be tapped after seven years' growth. But at this age the bark is so thin that certain precautions have to be taken in making incisions, and only the wheel pricker should be used. Plantation *Manihot* yields a rubber of good quality, but unfortunately only in small quantities, the average yield per tree not exceeding 18 ozs. per annum.

Castilloa, like *Manihot*, requires a very moist atmosphere, and grows very well in a permeable sandy clay; it can be tapped at ten years, but yields only the comparatively small amount of about 11 ozs. per annum. In consequence of these poor results the cultivation of *Castilloa* has been given up.

Whatever may be the actual position, and in spite of the very great difficulties of acclimatisation, plantation rubber has enjoyed very high favour in financial circles, and up to a point this confidence has certainly been justified by the results obtained in recent years.

In Malaysia, about 1910, there were no less than sixty plantation companies, representing a capital of £22,000,000; in Ceylon there were twenty companies, with a capital of over £3,000,000; in Sumatra sixteen companies, with a capital of £4,680,000; and in Borneo ten companies, with a capital of £400,000. The English capital invested in these different countries exceeded £34,000,000, and the yields were such that some companies were able to pay a dividend of 375 per cent.

In the Dutch East Indies there were, at the same time, more than two hundred companies, representing a capital of £22,500,000, of which £5,250,000 was provided by Holland, £15,000,000 by England, and only £2,250,000 by France and Belgium.

The area planted with *Hevea* and in bearing in June was 110,000 acres; in Ceylon, 200,000 acres; in Malaysia, 290,000 acres; in Borneo, 10,000 acres; in Sumatra, 80,000 acres; in British India, 30,000 acres; and in Samoa about 1,000 acres.

As *Hevea* does not yield much before the eighth year, the curve of exports is a very accurate picture of the progressive development of cultivation.

The imports into London, the chief market for plantation rubber, were as follows:—

	TONS.		TONS.
1905, ...	250	1908, ...	2,000
1906, ...	530	1909, ...	4,000
1907, ...	1,100	1910, ...	7,500

The progress is also reflected in the figures for the production in the different centres of cultivation. For Ceylon and British India the following figures have been given by the Government:—

	TONS.		TONS.
1906, ...	160	1909, ...	600
1907, ...	230	1910, ...	1,430
1908, ...	350	1911 (7 months), . .	1,220

For Malaysia, including Perak, Selangor, Negri Sembilan, and Pahang the figures were:—

	TONS.		TONS.
1906, ...	510	1909, ...	3,850
1907, ...	1,010	1910, ...	6,800
1908, ...	1,800	1911 (7 months), . .	4,649

Such results have not been obtained without great effort, and in the early days, in order to draw attention to plantation rubber, a vigorous advertising campaign was organised; to attract capital and facilitate the formation of big companies the earlier cultivations were almost sacrificed, the trees being tapped when only four or five years (sometimes even three years) old, in order at any cost to be able to get appreciable quantities of the new product on the market.

"Well presented," says Lecointe,[1] "this Plantation Para, as it was called, was declared to be superior to Para itself; the advance in values obtained led to an extraordinary infatuation, and a crowd of speculators and colonists laid hold of concessions of all the cultivable land in Malaysia. New enterprises were started by the hundred, somewhat at random; many of them disappeared in the maelstrom before they had so much as planted a single *Hevea*, whilst others already count their trees by the million. In brief, in July, 1910, according to the official report of W. J. Gallagher, Director of Agriculture, the capital engaged in the industry in Indo-Malaysia exceeded 37½ million pounds sterling, distributed between five hundred companies. This figure has since been almost doubled as a result of the second boom of 1910, and the total capital now employed in the Indo-Oceanic plantations may be estimated at 75 millions sterling."

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[1] *Caoutchouc et Guttapercha,* 1911, Sept. 15.

The production of these plantations is only just beginning to come on the market; in 1911 it totalled 14,000 tons, as against 38,000 tons produced by the Amazon region. But it will go on increasing rapidly, for a large proportion of the trees planted are not yet yielding, and will only begin to yield five or six years hence. Ferguson, of Ceylon, calculates that in 1915 Asia will put on the market a quantity of rubber equal to that provided by Brazil —viz., about 38,000 tons—distributed as follows :—

Ceylon, ...	12,000 tons.
Malay Peninsula, ...	20,000 ,,
Dutch East Indies, ...	6,000 ,,

This quantity will be doubled, it appears, in 1920, and this is highly probable, for the number of trees now exceeds 60,000,000.

According to the *Economiste Française* the figures for the Amazonian and the plantation production during the four years 1908-1911 are as follows :—

	AMAZON.	PLANTATIONS.
1908, ...	38,100 tons	2,200 tons.
1909, ...	38,980 ,, ...	4,000 ,,
1910, ...	36,270 ,, ...	8,000 ,,
1911, ...	38,000 ,, ...	14,000 ,,

In four years, therefore, the output of plantation rubber has shown a six-fold increase. If we compare these figures with those showing the export from the Amazon basin, it is almost certain that Ferguson's estimate is correct, and that plantation rubber has not far to go before its export will equal in amount that from the Amazon. M. Sorbier de Pougnadoresse, Chief of the "Consulat Général de France" in London, has reported that the quantity of plantation rubber now offered for sale there is sufficient for it to have had a beneficial effect, during 1911, upon the stability of prices. A "boom" similar to that engineered from Belem in 1910 is therefore no longer possible.

[That the forecast here given is not too optimistic, but errs rather in a contrary sense, is shown by the fact that the production of the plantations for the year 1916 amounted to 150,000 tons, that of the two preceding years being 96,000 tons (1915), and 64,500 tons (1914). The Amazonian output, on the other hand, remained practically at the same figure as in the years quoted above. For the year 1917 the plantation crop is estimated at 190,000 tons. As regards prices, the average for standard quality plantation rubber was about 2s. 10½d. per lb. in 1916, 2s. 6½d. in 1915, and 2s. 4d. in 1914. Conditions have, however, been abnormal during the greater part of this period.—T.R.S.]

Although the amount of plantation rubber exported has been continually on the increase, this has not been accompanied by a similar increase of profits, most companies showing a much lower net profit in 1911 than in 1910. This is due to two circumstances—viz., an appreciable increase in the cost of production and a drop in the selling price. The stage at which the production of the plantations has already arrived, and the position to which it must inevitably attain in the course of a very short time, have lent intense interest to the question of the competition between the two kinds of rubber.

In spite of the higher cost of labour, the total cost of production of plantation rubber is low; this cannot be said of wild rubber, as will be shown later. Still the increase in consumption, which in 1913 was really 1,000 tons per month, would hardly lead one to anticipate a fall in price. The event has belied many hopes.

As a matter of fact, before the synthesis of rubber was looked upon as possible, the enormous development which seemed to await the traffic in rubber in the far East was eagerly anticipated. This Asiatic product, obtained under, comparatively, very economical conditions, would, indeed, by competing with Para, gradually force down the price of the latter, and it was no longer the fear of not finding consumers for their rubber which would worry the other centres of production, but the unwelcome fact that they would not always be able to sell it at a remunerative price, on account of the high cost of production.

The contest, which has hitherto been a two-sided one between America and Asia, will, with the arrival of synthetic rubber, become triangular, and both natural producers will probably have to reckon with a third competitor. If the synthesis can be quickly and economically rendered commercial, a fall in price, in spite of a material increase in consumption, will inevitably take place to a figure as low as the cost of production of the natural product. This will probably come about slowly, as in the case of indigo, for preference will be given by manufacturers at the outset to the *Hevea* rubber with which they are familiar. The first result will be the elimination from the market of low-grade products, which have nothing but their low price to recommend them, and as the fall in price becomes more marked, rubber will come into use for a variety of industrial purposes, from which it is still excluded on the score of expense.

Whereas in the Indo-Oceanic regions there are something like 60 million *Hevea* trees which can be easily and cheaply worked—we shall go into the question of cost of production a little later—the Amazon district contains, at the lowest estimate, 200 million trees, or about three times that number, and, moreover, these trees have cost absolutely nothing, whilst the Asiatic plantations represent a capital outlay of about £120,000,000. The making of roads and railways, like the Madeira-Mamoré railway, now in process of construction, the removal of the exorbitant export duties, the suppression of local dues, the simplification of the methods of preparation, above all, the elimination of the *aviadores*—very costly middle-men—and the formation of companies with large capital to work the rubber, would combine to put Brazil in a position in which she might carry on a struggle with Asia under equal conditions, perhaps even with a slight advantage in her favour, for there the plant already exists and does not need to be grown. There will thus be a very lively struggle between the two natural producers, and, with good strategy, it is only after the exhaustion of these two combatants that the synthetic product should make its appearance on the market—the technicalities of its manufacture having been meanwhile worked out to the last detail of efficiency. The Germans, who have devoted most attention to this question, well understand this, and the book recently published by Ditmar gives expression to the idea with frank brutality. The fact is that, despite the slightly lower value of plantation rubber, as compared with Para, on the London market, future prospects would be superb if the estimated yields are realised, and if the price of 4s. 6d. per lb. were to be maintained. 35,000 tons of plantation rubber produced would, under these circumstances, represent a value of nearly £17,000,000, and as the capital invested is about £120,000,000, the interest yielded would amount to 10 or 12 per cent.

Will the arrival of synthetic rubber on the market interfere with the realisation of these hopes? Such a result would have a very serious effect upon the plantation companies and would jeopardise their capital before it could be written off.

In Indo-China, the French colony in which the authors are more particularly interested, the planters have not done at all badly, for there are to-day in the undertakings of Bellan, the Sussanah Company, Wathrohl, and Saint-Sauveur some 1,500,000 *Heveas* trees under cultivation; but although the red earths are quite suitable for the growth of rubber trees, the yields obtained are still very small. It is, however, pleasing to note, on referring to the work of Saint-Sauveur, Le Coupellier, Issaverdens, and Morange, that every day sees some fresh development in *Hevea* cultivation in Indo-China. It is thirteen years since the first half-hearted trials in connection with growing from seed were made at Ong-Glen, and the number of plantations has gone on increasing from that time, more particularly from 1906 onwards. This has been due as much to the care of the colonial administration as to the efforts of the colonists themselves.

The plantation of Phun-Nhan, which was established by Bellan, in 1899, now comprises about 110 acres, and is planted with some 15,000 trees, representing about 10 tons of rubber per annum. The Sussanah plantation, started by Cazeau, near Dang-Icey railway station, about 40 miles from Saigon, has an area of 770 acres, and contains 140,000 trees; Xa-Trach is 2,750 acres, and in addition there are plantations at Hiep-Kang, Phu-Quoc, Binh-Truoc, and Nuan-Loc; these are in the hands of some thirty companies, and comprise altogether about a million *Hevea* trees in full bearing.

These plantations may be classified into two groups. The first group includes the larger plantations which are situated in upper Cochin-China, on the fertile red earths, in districts which are entirely new, and recently opened up to civilisation. In these parts there would be about 1,000,000 acres suitable for cultivation, and of these concessions have been made of only 25,000 acres, at the very modest charge of 3d. to 4d. per acre per annum; the plantations are free from all taxation for a period of seven years.

The second group comprises the smaller plantations, situated within a radius of about 30 miles from Saigon, in districts which have long been under cultivation, and where the very sandy soil needs organic manures. This is the region of the grey earths, which are very much poorer soil than the red earths, but the district has the advantage of being nearer the ports and the commercial centres. The yields of rubber, as already stated, are rather poor, owing, more particularly, to the fact that the Indo-Chinese planters have copied the practice of their *confrères* in Ceylon, of beginning to tap the trees when they are only five years old.

Growth being less vigorous here than in Ceylon, it would have been better to wait until the trees were fully developed at, say, between seven and ten years old. According to Bellan a *Hevea* grown in Cochin-China only yields 5 ozs. of rubber at six years, 10 ozs. at seven, 21 ozs. at eight, 28 ozs. at nine, and finally about 2¼ lbs. at ten years.

Wickham considers these figures much too low, but they will doubtless be increased as the trees grow older. Labour is cheap in Cochin-China; a labourer is paid from 10d. to 1s. 1d per day, plus 28 ozs. of rice; cost of production is, therefore, low. Bellan estimates the total cost at about 1s. 1½d. per lb. in the case of a plantation where the cultivation of *Hevea* is combined with that of coffee, cocoa, and the sweet potato.

In Cochin-China, thanks to the annual dry season which kills off the spores, fungoid diseases are rare; it is this class of disease which is the pest of rubber plantations, and constitutes the one dark spot in their future. We have already seen that over-tapping causes the yield of even the wild *Heveas* of Amazonia to fall off and finally cease, and the same is true of the plantation *Hevea,* which is necessarily a less robust tree.

However similar the climates of two continents may appear to be, a plant transplanted from the one to the other requires to adapt itself more or less rapidly to its new environment, and in the course of this process the door is constantly open to a thousand and one mischances.

The most effective proof of the difference between the climates of Brazil and Indo-Oceania is perhaps furnished by the fact that *Castilloa,* which is abundant in the upper Amazon basin together with *Hevea,* cannot be cultivated in Malaysia, where it was thought it could be easily acclimatised. Moreover, it is not at all uncommon to find young, recently transplanted trees attacked and decimated by epidemic diseases which are very difficult to get rid of. *Hevea,* in Asia and Oceania, has met with a number of formidable enemies on the plantation, and their ravages are unhappily on the increase. It is attacked by several different fungi; *Fomes semitatus,* which attaches itself to the roots of young trees 15 to 30 months old, and *Corsum Javaniceum* which takes hold at the base of the branches, forming whitish patches, which become pink and increase in size, finally causing the bark to split, and bringing about the death of the tree. It is also liable to canker, which was found by Carruthers in Ceylon in 1903; this disease has been studied by Keith Bancroft.[1] Its presence is betrayed by an interruption of the flow of latex; the bark of the tree then blackens and the tree dies. The disease is caused by two parasites, *Diversis para nectria* and *Stilbella Hevea.* The former was described in 1909 by Petch, who found it on dead branches both of *Hevea* and tea, and classes it as a *saprophyte.* The *Stilbella* was investigated in Java in 1902 by Zimmermann. These two kinds of parasite have frequently been found on the incisions made in tapping. When the dead bark is removed the wood is seen to be discoloured, and the diseased tissue goes on spreading; it is necessary to excise the affected parts and to stop tapping; if the tree is healed—which happens but rarely—it cannot be tapped for several years.

Another enemy of *Hevea* to which reference must be made is the white ant, *Termes gestroi,* and it is of interest to note that this insect lives on quite good terms with *Hevea* in the Amazon district, whereas, on account of the character of the climate and the nature of the soil, it causes great damage in the plantations of Malay. Planters are at a loss to know the best way of dealing with this pest, which grows more troublesome every day, and against the depredations of which they are as badly protected as was France against the epidemic of phylloxera or mildew. There are other considerations helping to cast the shadow of uncertainty upon the somewhat too brilliant future which has been regarded as assured for plantation rubber; for example, from the industrial point of view, although it comes from the same tree as the Brazilian product, plantation rubber is not identical with the latter in properties, and consequently is not of the same value. There is nothing surprising about this fact; all plants, even those of the same species, derive from the soil in which they are planted characteristics which are peculiar

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[1] *Agricultural Bulletin,* Fed. Malay States, 1911.

to them as individuals; it is quite easy to understand, therefore, that plantation *Hevea* does not yield a rubber identical with that of the wild *Hevea* of Brazil.

The method of coagulation also stands for a good deal as affecting the value of the product. Wickham, who may be regarded as the creator of rubber plantations, having introduced the cultivation of *Hevea* into Ceylon, thinks that the processes employed in Asia and Oceania are worthless. Coagulation by acetic acid, as practised in Ceylon, or by means of alum or sodium chloride, as carried out in the Settlements and in Java, necessitate prolonged washing of the rubber in order to free it from excess of the coagulant, and this mechanical treatment of the rubber causes it to lose many of its good qualities. From the point of view of the product obtained no process is equal to that of smoking. The reasons for this can be readily comprehended, and they afford an explanation of the high esteem in which smoked rubber is held by the consumer. The latex is coagulated gradually in successive thin layers, and extraneous impurities cannot get into the rubber. On the other hand, the creosote present in the smoke exerts a powerful antiseptic action upon the putrescible nitrogenous substances in the latex, whereas in the acid treatment these latter are not rendered aseptic, and fermentation almost always occurs.

One of the least desirable methods of coagulation is that in which alum is employed; although one of the quickest, it distinctly impairs the elastic qualities of the rubber. In order, therefore, to make the most of the high quality of plantation rubber, coagulation by the method of smoking should be adopted in Asia and Oceania. This would necessitate training Hindus and Malays until they acquired the skill of the *seringueiro*, which, as Michelin puts it, almost allows of his signing his name to his product. Hence, in spite of the apparent success of rubber plantations, and of the favour they enjoy in financial circles, and notwithstanding the enormous amount of capital invested in them, they cannot be said to have definitely solved the problem of unlimited production of faultless rubber at a comparatively low price, and this because the quality of their products is often debatable, and because there are risks of fluctuations in yield on prolonged exploitation, and of other miscalculations resulting from cryptogamic tree diseases, with which we are not as yet thoroughly familiar.

CHAPTER II.

RESINOUS RUBBERS.

UNTIL within recent years rubbers with a high resin content were held in very low esteem. As was only natural, in the earlier days of rubber exploitation attention was paid only to the richest of the very numerous sources of rubber, and certain other kinds, where the actual rubber hydrocarbon was contaminated with a number of impurities, from which it could only be freed with difficulty, were disregarded, because they did not pay so well to collect and send down to the ports. These materials, formerly despised, to-day constitute a most important reserve, somewhat in the same way as the *Exbolades* of ancient iron mines, the waste residues of the Carthaginian, Greek, or Roman foundries, for which modern smelting works compete at high prices.

The resinous rubber which ten years ago was scorned is now much sought after, so much so that, as we shall see presently, Germany has, by means of a smart contract, succeeded in securing its principal source in Oceania, and created a monopoly in the production of *Jelutong*.

Speaking in general terms, all rubbers, whatever their origin, contain resins, not even excepting the purest among them, including Para itself. In most of the rubbers in common use these impurities are only present in traces, and are not troublesome in manufacture. But, as Chaplet and Rousset rightly state,[1] as soon as the amount of resin exceeds 4 per cent., it becomes impossible to work the rubbers conveniently. The resins melt, absorb sulphur, and the mass becomes brittle.

We ourselves have attempted to vulcanise a Jelutong containing 10 per cent. of resin, and have to admit that the vulcanised rubber obtained was absolutely useless.

Ditmar and Wagner[2] have shown that sulphur combines with resins up to a certain point, beyond which it remains free. They have found that on heating mixtures of Para rubber and Congo resin with increasing amounts of sulphur there is at first a continuous increase in the percentage of combined sulphur, but after a certain point the proportion begins to fall. From these prefatory observations the deduction can at once be made that the presence of resins lowers the value of rubber considerably, because they reduce its elasticity and suppleness, and through their imperfect blending with the mass render the latter heterogeneous, brittle, and friable.

According to Hanriot,[3] *Hevea* rubber, both wild and cultivated, and *Maniçoba* rubber, contain only a very small proportion of resins, and recent

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[1] *Caoutchouc et Guttapercha*, 1911, 8, Feb.

[2] *Chem. Zeit.*, 1907.

[3] *Revue generale des Sciences*, 1908.

analyses confirm their statements; Tonkin and Madagascar rubbers are notably richer in resins, but the rubber can still be separated by the ordinary methods. In *Guayule* rubber and the products of the Upper Congo, one has rubbers with a medium percentage of resin, and of poor elasticity, forming plastic, more or less pasty masses, and necessitating the use of special methods—which have actually been instituted in the case of Guayule—for separating the rubber hydrocarbon. Species of *Sapium*—viz., *Mexicanus* or *pedicellatum*—found in the north of Mexico, and others—viz., *Pleiostachys Adradenium* and *salciferum*—in Costa Rica, have been carefully studied by the American botanist, Pittier; they yield a latex with a lower rubber content even than Guayule, and the viscous coagulum from this has for a long time been used for no worthier purpose than as bird-lime; it is only quite recently that it has been studied with a view to the extraction of rubber from it.

The rubber-containing resins of Sumatra and the Dutch West Indies, in spite of their low rubber content (10 to 20 per cent.), are of much greater interest than the sticky, badly polymerised products of Gaboon, Flake, or Herat, which are often half-decomposed on their arrival in Europe, and the truly repulsive odour of which renders them so difficult to transport and to deal with.

According to David Hooper, who has devoted a great deal of attention to the various cultivated products of Ceylon, *Basnanian* rubber, extracted from *Ficus Cyngalensis*, is far superior to these products. It is a resinous mass, dirty white in colour, soluble in ether without swelling, and also in chloroform and carbon bisulphide; it contains 62·25 per cent. of various resins, and about 19·82 per cent. of rubber.

The same authority cites also as resinous rubbers *Mandar* rubber, obtained from *Callotropis gigantea* and *procera*, which contains 16 per cent. of rubber, and *Excœcaria* rubber, from *Excœcaria agallocha*, although the latter contains a large amount of albuminoid matter.

Faraday, and later Adriani, drew attention to *Cahutchu*, a resin from equatorial Africa, which contains from 10 to 30 per cent. of rubber, the remainder consisting of albuminoids, sugars, and wax.

Amongst Madagascar latices, so thoroughly studied by Jumelle and de La Bathie,[1] the following are worthy of attention:—*Bokabe* (*Mardsnenia Verrucosa*), *Adabo* (*Ficus Sakalavarum*), *Fiamo*, *Fosa*, *Fumato*, *Sefo* (*Adamsonia digitata*), *Sa Koa*, and *Tsitake*.

According to Cohen,[2] the resinous product which comes from the Ivory Coast under the name of African rubber, and which is obtained from a *Euphorbia* latex, must be regarded also as a rubber-containing resin. It is composed of 25 per cent. water, 5 5 per cent. rubber, and 70 per cent. of a substance closely allied to *cholesterol*, which is found amongst the resins of Jelutong.

We reproduce below the results of analyses by various workers, of these different kinds of rubber. The following were obtained by Fendler[3]: —

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[1] *Caoutchouc et Guttapercha*, 1911.

[2] *Bull. de la Soc. Chim.*, 1909, 798.

[3] *Moniteur scientifique*, 1905.

SOURCE OF RUBBER.	CAOUTCHOUC.	RESINS.	INSOLUBLE IMPURITIES.
	Per cent.	Per cent.	Per cent.
Para, crude, ...	63·3	2·1	34·6
Para, washed, ...	96·4	3·7	. .
Amazon (Euphorbia), ...	90·8	4·5	3·2
Upper Congo, ...	89·7	4·8	5·5
East Africa, Allem, ...	70·8	4·9	26·4
Java, ...	92·0	5·2	2·8
Sapium, ...	90·5	7·1	2·3
Cameroon, ...	70·1	9·6	19·8
New Guinea, ...	70·3	20·6	9·3
Borneo (purified), ...	72·2	24·7	3·1
Resinous (origin unknown), . . .	51·5	46·9	1·4

Terry and Weber obtained results which are rather different from the above. Terry's determinations were made by complete extraction, in a Soxhlet, with absolute alcohol. Weber obtained his results by dissolving 50 grammes of the rubber in a litre of crystallisable benzene, filtering the solution, and precipitating the caoutchouc with 2 litres of 95 per cent. alcohol. The resins were determined by evaporating the filtrate to dryness. They were found to consist of a mixture of neutral oxygen-containing compounds and acid substances, all soluble in alcohol or in alcoholic soda. This statement, cannot, however, be extended to include all rubber, because it is not true of the Jelutong resins, which are entirely insoluble in aqueous and alcoholic alkalies. With this reservation, the figures obtained by Terry and Weber are given in the following table :—

SOURCE OF RUBBER.	RESINS.		MELTING POINT OF RESINS.
	TERRY.	WEBER.	
	Per cent.	Per cent.	
Para, ...	1·2	1·3	5° C.
Ceara, ...	1·3	2·1	2° C.
Colombian, ...	2·5	3·8	. .
Mozambique, ...	3·0	3·2	18° C.
Rio, ...	5·8	5·2	64° C.
Madagascar, ...	6·1	8·2	. .
Sierra-Leone, ...	7·4	9·7	. .
Borneo (purified), ...	7·9	11·7	28° C.
Assam.	9·3	11·3	82° C.
Mangabeira, ...	10·5	13·1	48° C.
African Ball, No. 1, ...	18·5	22·8	38° C.
African Ball, No. 2, ...	22·8	26·1	20° C.
African Ball, ...	41·2	63·9	20° C.

Later, Fendler made other determinations, in which he used benzine as a solvent and precipitated the caoutchouc with alcohol: these later results differ considerably from his earlier ones :—

SOURCE OF RUBBER.	CAOUTCHOUC.	RESINS.	INSOLUBLE.
	Per cent.	Per cent.	Per cent.
Sernamby Para,	89·3	7·1	3·6
Maniçoba, crude,	92·0	6·3	1·7
West Indian scrap,	92·7	5·2	2·1
Mexico scrap,	91·4	3·3	1·3
Guatemala,	88·2	11·7	..
Madagascar,	78·1	17·6	4·3
Calabar,	92·5	8·0	..
Cameroon,	93·7	4·6	1·7
Upper Congo,	89·7	4·8	5·5
Mozambique,	50·8	2·3	46·9
Isambi,	89·8	6·2	4·0
Congo Thimbles,	58·1	3·0	38·9
Togo Manihot,	85·4	6·2	8·4
Borneo IA.,	87·2	8·6	4·2
Borneo IIA.,	72·2	24·7	3·1
Ceylon Para,	96·7	2·1	1·2
Bissao,	90·5	4·8	4·7
Java,	92·0	5·2	2·8

The most interesting of all these resinous rubbers, with the exception of the classical sorts, is "dead Borneo" or Jelutong. Fifteen years ago it was scarcely known, for it was at the Exhibition of 1900 that it was seen in Europe for the first time, in the Netherlands section. The Indies Mercury gave a few details concerning the product: it was derived from *Alstonia Costulata* (Miquel) or *Dyera Costulata* (Hooker), trees which were confused with one another under the name of Jelutong by the native Dyaks of the province of Pontianak, where they flourish exuberantly.

The composition of the product, as revealed by Von Romburg's analysis, is as follows:—15 to 20 per cent. of a caoutchouc deficient in elasticity, 30 to 40 per cent. of resins soluble in acetone, and 40 to 50 per cent. of water. Little was thought of the future of a product containing so low a percentage of rubber; it appeared, in fact, to be devoid of interest. It was classed below the *Almeidina* of Angola, and the *Sillan* of Caylor, Senegal, and the Congo, which, although highly resinous, seemed more capable of employment as guttapercha substitutes, owing to their resemblance to *Balata*. The rise in prices in 1910 attracted attention to Jelutong. Much energy was devoted to a careful, detailed examination of it, and investigators, practical men, and scientific men, such as Hanriot, Chaplet, Rousset, Robinson, Dreyfus, Gratz, Stechow, La Fresnaye, Combanaire, Poulverel, Worms, Flament, Joly, Dybowsky, devised a number of methods for effecting a comparatively easy and cheap separation of the rubber from the resins.

The quality of the rubber, after it has been purified by suitable means, is regarded by Markwell and Liebschutz as excellent; the resins have been repeatedly analysed, and found to resemble Gum Elemi very closely; they have, therefore, a substantial value.

Thus from being a product of negligible importance, "dead Borneo" has become a rubber worthy of being classed with others widely used; proof of this is afforded by its constantly increasing consumption. According to the *Straits Times* of Singapore the figures are as follows:—

1908,	62 tons.
1909,	191 „
1910,	248 „
1911,	6,000 „
1912 (estimated),	12,000 „

In addition to companies formed at the centres of production—companies with considerable capital like the "Sumatra Jelutong and Rubber Co.," the "United Malaysian Co.," and the "British Malaysia Co."—it may be imagined that in European centres this new rubber received its due share of attention. One can understand somewhat, also, the stir which was made about the formation of the "International Asiatic Rubber Co.," which set out to exploit Dybowsky's processes for isolating resinous rubber.

After a period of excitement lasting several months, during which companies for the exploitation of Jelutong sprang up on every hand, a period of somewhat greater calm set in. There were many reasons for this cooling off; however excellent a process may be, it is necessary, before attempting to exploit it, to make sure of being able to cover requirements in the shape of raw material, at prices within reach, and in sufficiently large quantity. Although there was a daily rise in price of the solvents generally used for extracting dead Borneo—acetone, alcohol, pyridine—on account of their increased consumption in a number of different industries, there was the expectation that the price of the principal raw material, the resinous rubber itself, would, on account of its superabundance on the market, always remain at a relatively low level. Not a great deal was known as to the number of Jelutong trees which were available, but, in view of the enormous increase in two years in the amount of the product exported, it was hoped that this might be increased a hundred-fold, and that still there would be almost inexhaustible reserves.

Our knowledge on such subjects as the cultivation of *Jelutong*, the methods of collection, and the prospects of future production, is still far from exact, and a great many people have risked their money in concerns founded for the treatment of *dead Borneo*, without even knowing whether the huge factories which it was proposed to put up would be able to obtain their raw material in sufficient quantity to keep them going. However, all fears of such a miscalculation would seem to be unfounded, according to the information conveyed in the very interesting account by Schidrowitz of his visit to the producing country.

However abundant the material may be, it is collected in a very rough and ready way by the Dyaks of Borneo and Sumatra; these natives evince the profoundest scorn for anything in the way of measures to safeguard the life of the trees. The classical methods of V- and spiral-tapping are not employed, but the thick bark is merely slashed with an axe, resulting, more often than not, in the death of the tree. It is understood that, faced with the rapid disappearance of the Jelutong forests, the Dutch Indies Government has adopted certain measures which will prevent the European and American consumers of the product from being taken by surprise. On the basis of the price of rubber in both continents, *dead Borneo* at 11s. to 12s. per picul (10s. per cwt.) at Singapore was certainly an interesting material, and it is easy to understand that attempts were made to establish a monopoly in it, various syndicates being formed for the purpose of obtaining sole rights from the Dutch Government for the exploitation of the trees.

One of these—the British Malaysian Manufacturing Company—was formed with the co-operation of American capitalists about March, 1910, and succeeded in obtaining an absolute monopoly from the Government of Sarawak.

At Kuching this company has a depôt at which the collection is centralised, and from which the products are sent on to Karimoun Island, near Singapore, where they undergo a purification which increases the rubber content to 60 per cent. At this stage they are exported to Europe and America. Towards the end of 1910 the same company obtained a further concession in the Federated Malay States, the new centre of the industry being Binasin.

About April, 1910, a French Syndicate was formed, and endeavoured to obtain a number of similar concessions. It does not seem that the very laudable efforts of their representative, M. Loiseau, were crowned with success. The most important group, which, in virtue of agreements with the various existing companies, and arrangements made with the Dutch Government, is to-day in possession of a true monopoly, is the United Malaysian Rubber Company, a German company with a capital of 50,000,000 francs (£80,000).

The granting of such privileges has not been unaccompanied by very vigorous protests in several quarters; it amounts, indeed, to a forcible seizure of the rights of exploitation of a very abundant source of rubber—a source upon which many had based their calculations—and the monopolisation of which renders the success of the numerous campanies which have been formed in Europe for the treatment of resinous rubbers very precarious.

None the less, the United Malaysian Company has certain very heavy charges to carry, and these will, for a time, diminish its prosperity: for instance, it is under an obligation to purchase from the British Malaysian Company its extraction processes, its factories, depôts, and concessions. As a set-off it has enormous advantages.

Being anxious to save the rubber forests from the destruction with which they are threatened as a result of the barbarous methods employed by the Dyaks, the Dutch Government entered into an agreement with the German company, which should have been in operation since March, 1911, and of which the fundamental points are explained below.

The Dutch Government grants the United Malaysian Company a lease of thirty years on $6\frac{1}{4}$ million acres—about 3 million hectares—of forest land—that is to say, the whole of the land in the Dutch East Indies on which Jelutong trees are likely to be found.

In principle the exploitation must be so carried on that the trees are not bled to death, and that in case trees are destroyed they shall be immediately replaced, under a penalty of ten florins per Jelutong tree.

The whole of the territory conceded must be brought into working within six years, one-tenth to be worked in the first year and an additional one-fifth in each of the four succeeding years.

The company shall put up a sufficient number of factories to be able to purify the whole of the Jelutong collected to the extent of leaving 60 per cent. of rubber in the product, and no rubber above this figure may be exported. The concession may be revoked by simple denunciation, without the intervention of any judicial authority, and damages may be claimed, if any of the terms of the contract are not observed.

The United Malaysian Company undertakes to pay for the Jelutong collected by the natives at a certain minimum rate.

In short, as will be seen, this contract gave Germany full control over the richest centre of production of resinous rubbers in the world, and that at a time when the product was just coming into use.

Such a treaty has called forth numerous protests, and it has been strongly criticised by M. Schlimmer, Director of the Borneo and Sumatra Handel Maats Chappij.[1] Such criticisms from a man on the spot, and thoroughly conversant with the whole subject, are well worthy of close attention.

M. Schlimmer contends that the concessionaire company will be utterly unable to fulfil the terms of the first clause of the contract, the object of which is to preserve the wealth of the forests conceded to it, because numerous experiments have demonstrated :—

(1) That the only way to make exploitation pay is to adopt the barbarous methods employed by the Dyaks.

(2) That re-plantation is impossible from the character of the soil.

In order to achieve the desired result, it would be necessary to insist on the adoption of methods similar to those employed in Sarawak ; but the Government has not troubled about that, any more than it took the trouble to make a serious survey of the territory which it was conceding.

On account of the marshy character of the country, it would not even be possible in six years to count the trees on it. Simply to penetrate the forests would necessitate the making of roads and canals, which would swallow up the whole of the company's capital, and occupy them for the whole period of the concession.

M. Schlimmer concludes by saying that the Government of Dutch East Indies has committed a grave error, and will not, in his opinion, derive much benefit from a contract which places the richest asset of the country in the hands of foreigners.

Thus the chief source of resinous rubber, as to the abundance of which high hopes were rightly entertained, is now, if not actually dried up, at any rate directed into particular channels by skilful hands which will be capable of making it serve their own ends.

Schidrowitz, in his "Journey through Malaysia," has given much interesting information about *Jelutong*, especially as to the methods of collection and of purification employed. The gum is obtained chiefly from the *Dyera costula'a*, a tree which is abundant in the forests of Sarawak, South and Central Borneo, and Sumatra, and is also met with in the Palembang and Pontianak districts. In those districts alone which have been prospected, and which are really comparatively unimportant, the number of trees noted is sufficient to ensure a production of 30,000 tons. An unexaggerated estimate of the possibilities of the less known portions of the Dutch Indies would give for the time when all the trees are being dealt with a quantity of 90,000 tons of the gum, or 18,000 tons of rubber. Mature trees attain a diameter of from 4 to 6 feet, and they are not tapped until they have reached this size.

The average yield of latex per tree per tapping varies from 1 kilo to 1½ kilo ; in practice the tree is tapped once a week, or fifty times a year. The latex contains from 15 to 20 per cent. of *Jelutong*, a mixture of resins and rubber ; it is coagulated by means of kerosene or petrol. Various powders containing copper sulphate, alum, and gypsum, supplied to the Dyaks by Chinese traders, are also added.

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[1] *Straits Times*, Singapore, Mar. 1911.

The coagulant is added to the latex a little at a time, the whole being kept constantly stirred; to every picul of latex 2 gallons of kerosene are usually added—that is, about 18 litres to 120 kilos.

Jelutong comes on the European markets to some extent in its crude form, but in 1911 it was difficult to find more than 200 to 300 tons; the whole production is, as has been said, collected at Kuching, and afterwards refined either at Karimoun or Goebilt. The daily production of these factories is about 15,000 kilos (15 tons). Here the gum is enriched to a 60 per cent. standard. The only impurities removed in the process are, practically, salt water and resins, and it is necessary to still further purify the product at the factory on which it is to be used.

In order to carry out in the most efficient manner the separation of the rubber from the resins with which it is contaminated, a complete analysis is necessary, and on the results of this will depend the choice of the solvent to employ in the separation process.

Generally speaking, rubber resins occur as somewhat complex mixtures, which, up to now, have been very little investigated; only their general characteristics are well known.

Hinrichsen and Marcusson[1], for example, observed that certain resins were optically active, whilst others had no effect upon a beam of polarised light. Their observations are summarised in the following table:—

HINRICHSEN AND MARCUSSON'S TABLE.

SOURCE OF RUBBER.	OBSERVED ROTATION, α_D.	SPECIFIC ROTATION IN BENZENE SOLUTION, $[\alpha_D]$.	PROPORTION OF UNSAPONIFIABLE CONSTITUENTS.
			Per cent.
Para,	0	0	15·0
Ceylon,	0	0	20·8
Congo,	+ 13°	+ 0·12 to 0·13	56·6
Dead Borneo,	+ 50°	+ 6·92 to 7·02	100·0
Padang,	+ 29·4°	+ 0·35 to 0·36	90·2
Guayule,	+ 12·5°	+ 0·32 to 0·59	78·2
Massai,	+ 29·8°	+ 0·55 to 0·58	92·2
Kickxia,	+ 32·9°	+ 0·98	74·0
Gutta,	+ 46·7°	+ 1·81 to 1·84	83·6

Those resins which have a high specific rotation are saponifiable to only a slight degree; those, on the other hand, which contain large proportions of saponifiable constituents are only slightly active.

According to Burghardt,[2] the rubber resins owe their formation to a chemical change undergone by the rubber, under atmospheric influence, while in a state of suspension in the latex. Two resins are formed, one, a highly oxidised product, optically inactive and soluble in alkalis, is similar in its properties to abietic acid, whereas the other is unsaponifiable and soluble in benzene, alcohol, and ether.

These resins, according to Otto Korneck, yield, when treated with ozone, an ozonide quite different from that of rubber. It is not converted into

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[1] *Caoutchouc et Guttapercha*, 1911.

[2] *Moniteur Scientifique*, 1904.

levulinic aldehyde by the action of water, and it is soluble in carbon tetrachloride. The formation of such a derivative would seem to offer a rapid method of determining the resins in a rubber.

Korneck's data have, however, been called in question by several chemists.

Wagner[1] records that the resins of the Congo rubbers are soluble in alcohol, ether, acetone, benzene, chloroform, petroleum ether, carbon tetrachloride, carbon bisulphide, ethyl acetate, dichlorhydrin, nitrobenzene, and glacial acetic acid; strong sulphuric acid produces a red colouration with a green fluorescence; in fuming nitric acid the resins dissolve, and, on dilution with water, yellow flakes are precipitated from the solution. According to Hanriot, rubber resins are only sparingly soluble in ethyl and methyl alcohols. Robinson, Dreyfus, Friedel, and Bentley state that pyridine and analogous bases are very good solvents, whilst alcoholic soda or potash have little solvent action.

According to La Fresnaye, the best solvent for the resins is acetone, which possesses the advantage of being easily recoverable by distillation. Hanriot proposed to use a mixture of solvents for effecting a separation of resins from rubber; by acting on both rubber and resin with solvents the complete solution of the latter is more readily effected. For example, a rubber resin which when treated with acetone at 20° C. only dissolves to the extent of 40 grammes per litre, is soluble to the extent of 240 grammes per litre in petroleum ether (sp. gr. 0·650) at the same temperature.

Using a mixture of 4 volumes of petroleum ether and 3 volumes of acetone at 23° C., 250 grammes of rubber resin pass into solution.

These results are similar in all points to those obtained by Coffignier in the case of tannin, but it is not correct to suppose that, in the case of *Jelutong*, the rubber is not dissolved.

In our experiments we obtained the following results:—*Jelutong*, which has been previously swollen in carbon tetrachloride, dissolves in the petrol-acetone mixture in two hours at 15° C. It gives a milky solution, which can easily be filtered, and from which the rubber can be precipitated in a pure state by the addition of pyridine or ethyl ether. To obtain a good result the fraction of petroleum ether distilling at about 100° C. must be employed. Rubber resins, and, in particular, those of *dead Borneo*, are also soluble, on the authority of Bottler, in methyl acetone, terpineol, chloral, and "l'huile de terpine."

Steglitz's method for the determination of the resins is based upon these observations. The method consists in dissolving the rubber previously dried in a vacuum over sulphuric acid, in petroleum ether (B.P., 60° C.), filtering the solution, and precipitating the rubber by means of a mixture of alcohol and acetone. The resins are isolated by evaporating the liquid to dryness.

Below are recorded the results of analyses which we were led to make of crude *Jelutong*, just as it leaves the hands of the Dyaks, before it has been purified in any way. The crude *Jelutong* forms a whitish, crumbly mass, easily compressed between the fingers, and having a characteristic odour, very different from that of the African resinous rubbers.

When the mass is chopped up and pressed about 25 per cent. of its weight of a whitish liquid, similar to watered milk, exudes. Microscopic examination

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[1] *Gummi Zeitung*, 1907.

reveals the presence of a few strings of flattened, colourless globules. When filtered the liquid is yellow and smells of iodine ; it reacts with silver nitrate, barium chloride, and potassium biantimoniate, and leaves a residue amounting to 0·22 per cent. of its own weight on evaporation. It appears to be made up of sea water holding a little resin in suspension.

When dried at 110° C. to constant weight it was found to lose, as follows :—

Outside layers, ...	38·63 per cent.
Intermediate layers, ...	42 „
Central layers, ...	43·25 „

However, when dried in a vacuum over sulphuric acid *Jelutong* resin loses only 32·7 per cent., and it would, therefore, seem that some 6 per cent. of the water is chemically combined.

The dried mass is brown, very crumbly, and much more like a resin than a rubber ; it is then only sparingly soluble in acetone. It leaves, on ignition, 0·66 per cent. of ash, containing silica, lime, magnesia, and sodium chloride. Exhaustive extraction, with acetone, of the dried *Jelutong* gave figures for resins varying from 72·80 to 85·89 per cent.

Hence the composition of the crude, undried product appears to be as follows :—

Water, ...	43·25 per cent.
Rubber, ...	7·11 „
Resins, ...	48·98 „
Mineral Matter, ...	0·66 „
	100·00 „

By Hanriot's method—solution of the substance in a mixture of petroleum ether and acetone, followed by precipitation of the rubber by pyridine or ethyl ether—a very pure rubber, easy to dry, and exceedingly elastic, is obtained, and by this method we obtained the following results with three samples of the product :—

	SAMPLE.		
	A.	B.	C.
Water, ...	43·2	43·4	45·2
Rubber, ...	19·2	17·4	12·6
Resins, ...	36·9	38·3	41·8
Mineral matter, ...	0·7	0·9	0·4

When first separated the rubber is quite white, but it rapidly becomes brown when exposed to the air, probably on account of the presence of oxidases.

It contains only a small amount of oxidised rubber, according to Weber's test.

It reacts with ozone, by Harries' method, to form an ozonide, which is decomposed by water into levulinic aldehyde and levulinic acid, and it readily forms nitrosites and bromides.

It can be vulcanised quite readily, by both the hot and cold processes, and yields vulcanised products with good nerve and highly elastic.

The resins are recovered from the solvent by distillation, and may be separated as follows into two constituents, both of which are optically active and unsaponifiable. The residue which remains after the solvent has been removed is treated with hot acetone, when a part (resin A) dissolves; the remainder is taken up with petroleum ether and crystallised from it (resin B). The elementary composition of these two isomeric resins is :—

Carbon,	84·6 per cent.
Hydrogen,	12·2 ,,
Oxygen,	3·2 ,,

and is very close to that of *Gum Elemi* and also of cholesterol, with which substances, moreover, they possess a number of characteristics in common. Their molecular weight is 402, and their empirical formula appears to be $C_{25}H_{50}O$. Their behaviour towards various solvents and reagents is shown in the following table :—

SOLVENT OR REAGENT.	RESIN A.	RESIN B.
Ethyl alcohol, absolute,	Insoluble.	Insoluble.
,, dilute,	,,	,,
Methyl alcohol,	,,	,,
Amyl alcohol,	Soluble in the hot.	,,
Acetone,	Soluble.	,,
Ethyl ether,	,,	Soluble.
Benzene,	,,	,,
Chloroform,	,, giving yellow solution.	,, without colour.
Petroleum ether,	Soluble.	Soluble.
Carbon tetrachloride,	,,	Slightly soluble.
,, bisulphide,	,,	,,
Acetic acid,	Soluble in the hot.	Insoluble.
Formic acid,	,,	,,
Propionic acid,	,,	,,
Butyric acid,	,,	,,
Nitrobenzene,	,,	,,
Pyridine,	Slightly soluble.	Slightly soluble.
Terpineol,	,,	,,
Aniline,	,,	,,
Amyl acetate,	,,	,,
Turpentine,	Soluble.	Soluble.
Bases,	Insoluble.	Insoluble.
Chloral hydrate,	Soluble.	Slightly soluble.
Fuming nitric acid,	Soluble in the hot, yellow flakes.	Slightly soluble, white flakes.
Sulphuric acid,	Red colouration.	Green fluorescence, brown colouration.

The two resins have the following melting and boiling points :—

	M.P.	B.P.
A,	80°	195°
B,	105°	210°

The resins may be distinguished from one another by—

(1) Their melting points.
(2) Their solubility in acetone.
(3) Their reaction with nitric and sulphuric acids

Resin A is readily esterified by heating it with organic acids.

It is possible that these resins, like cholesterol, are secondary ethylenic alcohols.

Let us now see how the facts just summarised have been applied to industrial processes for dealing with resinous rubbers.

The processes of deresinification, as at present practised, may be divided into two large groups :—

(1) *Complete solution processes*, in which the whole of the rubber and resins is dissolved, the rubber being afterwards precipitated by a precipitant which does not throw down the resins.

(2) *Extraction processes*, which may again be subdivided into two groups :—

(*a*) In which a solvent is employed which dissolves the resins only; and

(*b*) In which a mixture of solvents is used, one to swell the rubber and the other to dissolve the resins.

In case (*a*) the rubber is repolymerised, or restored to its original unswollen condition, by treatment with a precipitant in which resins are soluble.

Type (1) process is represented by the method of Gratz, who uses as solvent either benzene, petroleum ether, turpentine, or carbon bisulphide, and precipitates with a mixture of alcohol and acetone. In this case resin B remains behind in the rubber.

Folsing's process is carried out in two stages :—

(1) Solution of the resins in acetone.

(2) Solution of the partly purified rubber in benzene, and reprecipitation by means of alcohol and acetone.

The drawback to the complete solution processes is that they yield viscous, inelastic products, the rubber being partly depolymerised, and requiring to be treated with halogen acids in order to restore its original properties.

With the exception of Gratz's process, in which aniline is employed as solvent for the resins, all the extraction processes require the use of acetone, either alone, as in Poulverel's process, or in admixture with alcohol or pyridine. They differ from one another mainly in the mechanical devices employed to enable the solvent to reach the resins effectually. Such are the processes patented by Stechow, by "La Société belge de raffinage," by Combanaire, and de la Fresnaye, by Worms and Flament, and by Chaplet and Rousset, of which the last-named seems to be the most practicable and economical.

Dybowski, in the patent which he has assigned to the Asiatic Rubber Company, employs either a mixture of alcohol and ether, or carbon bisulphide to swell the rubber, the pasty mass being then worked with acetone and alcohol to extract the resins, and afterwards subjected to a methodical extraction, so that at the end there is left only a granular rubber, which can easily be dried.

CHAPTER III.

RECLAIMED RUBBER.

In order to meet the immediate requirements of the world in rubber, many attempts have been made to restore to a useful condition waste material and worn-out or discarded articles, just as is done in the case of steel, iron, and brass. On this analogy, although a piece of hose or a rubber joint may have ceased to serve its original purpose, or a tyre may be perished, the rubber contained in them, together with the loading materials, will not have been radically affected; hence if the rubber can be separated from them and restored to its original state as regards flexibility and "nerve," a regenerated product will have been obtained which, in quality and value, will be able to compete with the natural product, and be to a great extent used in place of it. It is, therefore, reasonable to study very closely the conditions under which the reclaiming of waste rubber is possible, and to try and ascertain whether those conditions will permit of the production of a material at a price sufficiently low to make it a serious competitor with synthetic rubber.

For reasons to be explained later, this programme has not been able to be carried out except in a very fragmentary way.

The delicate industry of reclaiming, which is centred in America and Germany, has not up to the present made a very powerful impression on the market. Alexander, one of the chemists who know most about this difficult subject, admits that the problem is very far from being solved, and even if it were, the economic conditions surrounding it are such that its interest is only small.

Although innumerable patents have been taken out, no one seems to have succeeded in effecting a perfect regeneration of rubber One reason for this is that in investigations of this kind the fact has too often been overlooked that, in Gerber's phraseology, natural rubber behaves as if it were an actual living substance, and that, further, it is a colloid in the behaviour of which it is difficult to distinguish between physical and chemical phenomena. We shall have to return to a fuller consideration of this question later, when dealing with the synthesis of rubber.

In the case of reclaimed rubbers, the matter is complicated by the fact that the original rubber has been altered in its properties by the heavy mechanical work which has been done upon it. All the evidence points to the conclusion that just as the steel of a locomotive axle undergoes a molecular change while in use, so the rubber of a tyre experiences a change of structure as a result of its continual rolling over the ground. Prolonged mastication, combined with a high temperature, during the mixing process, have already lowered the degree of polymerisation, and injured some of the initial properties of the rubber, more especially its "nerve." Vulcanisation, on the other hand. can only fix, or stabilise, its properties to a limited extent.

Then, again, rubber is not, as one might be tempted to believe, a substance which is indifferent to the action of reagents; sulphuric, hydrochloric, and nitric acids attack it slowly, as do also soda and potash; it is oxidised by oxygen and ozone, and undergoes a species of degradation under the influence of light, more particularly the ultra-violet rays, as well as of oxidases and peroxidases; its valuable and characteristic properties are profoundly modified by these influences.

As already explained, the effect of mechanical work done on rubber is to enhance the above destructive effects, so that it is upon a substance which is partly decomposed, which has undergone a variety of deep-seated changes, both chemical and physical, and the equilibrium of whose complex molecular structure has been disturbed, that the reclaiming process has to be carried out. But even if the rubber had not been subjected to these destructive influences, the problem of its isolation from the complex mixture which constitutes a commercial rubber would be none the less difficult. The detailed study of these questions, by M. Masselon, published in *Le Caoutchouc et la Guttapercha*, shows how very important they are.

The first stage of the process, and one of the most delicate, is the removal of the sulphur, free and combined; and although the former can be easily extracted by acetone, or by alcoholic soda—which also dissolves the vulcanised oil substitutes incorporated in the mixing—it is not so with the sulphur of vulcanisation. Whether the latter is present in definite chemical combination with the rubber, or whether, as Ostwald holds—against much opposition—in the form of a colloidal solution in the rubber—that is to say, whether we are dealing with combined or adsorbed sulphur, the fact remains that the extraction of the sulphur is a difficult and tedious process. The union between sulphur and rubber is of so firm a character that, when the nitrosite or the bromide are prepared by the action of nitrous acid or of hydrobromic acid on the vulcanised substance, the sulphur reappears in the new compounds, a fact which is liable to give rise to serious errors on analysis. Although Ostwald's opinion carries great weight, there is good reason to believe, with Weber, that vulcanised rubber is an addition product. By reason of the colloidal character of rubber, not only its chemical but also its physical state is influenced by the formation of these addition products; their presence has a determining influence upon changes in the degree of polymerisation, bringing about, according to circumstances, an increased complexity or a degradation.

The rubber hydrocarbon is very easily affected by the most diverse influences, being broken down into molecules of smaller size, or forming higher aggregates as the case may be. In this circumstance we have the key to the problem of vulcanisation, and, without at this stage going into all the details, it is necessary to give it some attention from the point of view of "reclaiming."

It may be laid down as a guiding principle, that to every different state or condition of the vulcanised product, and to every amount of sulphur fixed, there corresponds a definite equilibrium between free sulphur, free rubber $(C_{10}H_{16})_n$ and vulcanised rubber $(C_{10}H_{16}S_2)_n$, and that this system is possessed of certain definite properties. On this assumption, if we attribute to natural rubber the degree of polymerisation $(C_{10}H_{16})_{20}$, we have, between this product and ebonite, which appears to be a compound of rubber saturated with sulphur, a whole series of polyprene sulphides; the number of possible systems in equilibrium is, therefore, very great. This does not render the problem of reclaiming any easier of solution, for logically every system dealt with would demand special treatment. Such a solution is hardly a practicable one industrially, and a desire to apply it would lead to the conclusion that the reclaiming industry had reached a deadlock.

For these reasons, and others of a purely empirical order, operations in practice are limited to attempts to reclaim lightly vulcanised rubbers; these soft rubbers, in which, apparently, a large number of unsaturated linkages still persist, have only been partially attacked by the vulcanisation process, and the system in equilibrium corresponds very closely to the initial system. Under these conditions a rubber can be recovered which, if not to be compared with the natural product, is at least capable of being used in a mixing in which natural rubber is the principal ingredient, especially if the "reclaimed" has been freed from free sulphur and loading materials. It is, then, rather as a "compound" or loading material of a special character that reclaimed rubber can be employed; used by itself it gives inferior products, and can only be employed for the lower classes of goods, such as jointings or toys.

Alexander has, very correctly, defined reclaimed rubber in the following way:—"A product prepared from soft rubber waste, and differing from it by reason of a higher content of rubber hydrocarbon and a greater degree of plasticity." This increase in rubber content can only be brought about by removal of the loading materials, and, if possible, by actual devulcanisation—that is to say, it is a chemical problem. The greater plasticity can only be obtained by some alteration of the molecular grouping—that is to say, either by polymerisation or depolymerisation, according to circumstances. It is, therefore, a physical or, at any rate, a physico-chemical problem.

We will consider these two aspects of the problem in turn.

It is a comparatively simple matter to remove free sulphur from soft rubber which has been finely ground, and apparatus is in existence for the purpose of accomplishing this rapidly and economically. Henriques and, later, Weber, for example, suggested the use of alcoholic soda at 75° to 80° C.; under this treatment the free sulphur is converted into sulphide, and is removed from the rubber as such. Rubber which contains very little loading material—*e.g.*, grey inner tubes—can in this way be rendered fit for use in mixings again without further treatment.

But in addition to alcoholic and aqueous soda many other reagents have been suggested which are capable of removing the free sulphur, either through the formation of polysulphides—*e.g.*, calcium sulphide and the hyposulphites used in Theilgaard's process—or through the formation of sulphides, as in the use of finely divided metals.

The following is a list of patents on this subject, and to these the reader is referred for details:—[1]

SODA-LIME-BARYTA.

Broomann, *Eng. Pat.*, 90, 1855.
Ford, *Eng. Pat.*, 2,090, 1855.
Alexander, *Eng. Pat.*, 25,735, 1906.

ALKALI CARBONATES AND SULPHIDES.

Anderson, *Eng. Pat.*, 18,008, 1898.

SOAPS.

Broomann, *Eng. Pat.*, 90, 1855.

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[1] *Revue de Chimie pure et appliquée*, 1912, 267.

Aniline and its Homologues.

Gregory, *Eng. Pat.*, 8,378, 1905.
Chodrowsky, *Fr. Pat.*, 409-432, 1909.

Metallic Powders.

Michelin, *Fr. Pat.*, 233,031, 1893.
Bary, *Fr. Pat.*, 415,213, 1909.

Sulphides of Iron, Lead, and Copper.

Bary, *Fr. Pat.*, 413,809, 1909.

Metallic Oxides.

Bary, *Fr. Pat.*, 415,213, 1909.

Metallic Peroxides.

Debauge, Addition to *Fr. Pat.*, 413,809, 1910.

Lead Acetate.

Kenler, *Fr. Pat.*, 313,747, 1901.
Chautard and Kessler, *Eng. Pat.*, 8,084, 1902.
Bary, *Fr. Pat.*, 415,213, 1909.
Bongrand, *Fr. Pat.*, 407,146, 1909.

These desulphurising compounds are employed sometimes before the rubber is dissolved, as in the case of the alkalies, carbonates, sulphides, sulphites, aniline and its homologues, and sometimes after solution, as in the case of the finely divided metals, metallic oxides and peroxides, salts of lead, and certain metallic sulphides. In the latter class, the lead salts seem to be the most interesting.

The complexity of the problem of separating rubber from sulphur and "compounds" is different in the cases of pneumatic tyres, red inner tubes, outer covers, rubber toys, goloshes, and washers.

The cost of these various types of waste rubber, on the Paris market, is a fairly true indication of their intrinsic value from the standpoint of rubber content, and it will, therefore, be of some interest to quote figures.

PRICE PER CWT.

Bicycle tyre outer covers,	£0	16	0
Smooth motor tyre covers,	1	13	0
Motor tyre covers with iron and copper,	0	19	0
Grey floating inner tubes,	10	0	0
Grey "semi-floating" inner tubes,	5	0	0
Red bicycle inner tubes,	4	8	0
Red motor inner tubes,	5	16	0
Solid tyres,	2	12	0
Goloshes,	0	17	0
Grey and drab toys, without fabric.	0	17	0
Black toys,	1	10	0
Ordinary toys,	1	0	0
Washers,	4s. to 10s.		

Hose, valves, and other forms of rubber used in the factory fetch still lower prices—viz., between 2s. and 14s. per cwt. These differences of price are regulated by the content of pure rubber and of "compounds," and by the physical condition of the waste rubber and the consequent greater or less difficulty involved in the reclaiming process. Moreover, the value of these different grades can be determined by analysis. Grey, floating inner tubes contain, by analysis, 80 to 85 per cent. of rubber, scarcely any free sulphur, and a little magnesia; by treatment with acid, followed by alcoholic soda, a rubber can be recovered from them with physical properties very little different from those of the original rubber; hence the high price of this class of goods is perfectly justified. Red inner tubes contain antimony sulphide, which can only be separated by a very delicate process, and at a fairly high temperature, after very careful grinding. The rubber is considerably altered during the working, and remains slightly tacky even after washing repeatedly with alcohol and acetone.

The value of an old outer cover is only one-sixth of that of an inner tube; an analysis of a Michelin tyre showed that, assuming that the pure rubber could be extracted and brought back to a condition in which its original properties were restored, the rubber would work out, after allowing for the whole cost of extraction, at about 2s. 2d. per lb. The price paid for the waste—33s. per cwt.—although at first sight very low, is, on the other hand, excessively high, and it is difficult for a manufacturer to make the treatment of such a product pay.

Solid tyres are of still poorer quality, the non-rubber present reaching as high a figure as 63 per cent., and the rubber content falling as low as 10 to 12 per cent.; in shoe-soles the proportion of rubber is somewhat higher —viz., 20 to 25 per cent.—the non-rubber being about 36 per cent. Valves, hose and gas tubing, and toys contain only a few per cent. of rubber, and are not worth treating.

Since the free sulphur is extracted by means of alcoholic soda, or aqueous soda under pressure, the fabric present must be destroyed, and with this end in view the crushed waste is soaked in an acid-bath, which removes such fibres as have not been removed by the air-separation process.

This process is a rather delicate one, and every acid is not suitable; in fact, certain acids, as we shall see later on, such as hydrochloric and nitric, are liable to combine with the rubber, forming products which are quite insoluble in the usual solvents. In practice, therefore, one is limited to the use of sulphuric acid, which has little tendency to combine with the rubber.

To be on the safe side, it is generally better to use caustic soda, which converts the cellulose of the fabric into pulverulent hydrocellulose, or to employ other solvents of cellulose, such as zinc chloride or cuprammonium.

Ever since rubber became an object of attention—that is to say, for the last 170 years—but more particularly during the last decade or two, during which the consumption has developed so remarkably, very many solvents have been suggested for bringing it into solution, but in no instance can an absolutely perfect and practical one be said to have been discovered.

As early as 1750 La Condamine wrote, with reference to the experiments on solution made by Fresneau at Cayenne:—"M. Fresneau has tried to dissolve rubber by a number of methods. But whereas I met with no success, although I tried, not only water, but various spirituous liquors, he has been more fortunate, and has actually produced a solution by warming the rubber with nut oil for a long time over a fire or on a sand-bath." Later on, in 1758, referring to the experiments made by Macquer and Hérissant with the same object, La Condamine again wrote:—"The ordinary resins do not dissolve in water, and in this respect rubber resembles them, but it differs in being insoluble in spirits of wine. It is attacked by neither of these solvents; it is, however, softened and gradually dissolved by nut oil or olive oil, but does not recover its solidity nor its elasticity." As regards this particular point the problem remains as it was, for a regenerated rubber never completely recovers these two properties. Macquer, Hérissant, and Bernard employed Dippel's oil, turpentine, or camphor vapour as solvents, and since then benzene, nitrobenzene, chloroform, various terpenes, petroleum ether, pyridine, cymene have been tried, together with a large number of other aliphatic and aromatic compounds, but the ideal solvent has not yet come to light. Such an ideal solvent will possess the following properties; it will be capable of rapidly producing a concentrated solution of rubber which can be filtered with the aid of existing forms of filtering apparatus, and will be capable of producing such a solution at low temperatures in order to avoid the risk of bringing about those changes in molecular complexity which invariably result from the application of heat to rubber.

The list of solvents is a very long one, and includes turpentine, terpenes and their derivatives, caoutchene, isoprene, hevèene, terpinol, terpineol, limonene, eucalyptol, resins, petrol and naphtha, paraffins, vaseline, benzene, toluene, xylene, creosote, tar, phenols, naphthols, naphthalene, pyridine, nitrobenzene, animal oils, vegetable oils, camphor, fats and stearin, carbon disulphide, ethyl chloride, methyl chloride, carbon tetrachloride, chloroform, ethers, etc. Unfortunately there is not a perfect one amongst them.

A complete list of patents which have been granted in connection with the solution of rubber in various solvents is given at the end of this chapter. Most of these patents are of little value, since numerous anticipations of them are to be found in various scientific works published since the time of La Condamine. The patents are not of equal value, and it might be advantageous to employ one or other of them in preference to some others on account of the method described for recovering the solvent. Speaking of them generally, it may be noted that the most active solvents are not, as a rule, the best, because their great affinity for the rubber renders their ultimate separation from it very difficult.

As a matter of fact, we find that results can only be obtained with the solvents employed in reclaiming practice by raising the temperature, frequently to a point at which the rubber begins to decompose.

The solution, or pseudo-solution, obtained is composed of (1) the dissolved rubber—or, at any rate, the "jellified" rubber—in the form of a *sol*; (2) loading materials in suspension. The latter must be separated from the rubber solution mechanically: filtration, either in the filter press or on porous plates, is not a success, and yields only very incompletely purified products.

On the other hand, the use of the hydro-extractor enables the loading materials to be easily separated. They are driven outwards against the walls of the bucket, whilst the solution of the purified rubber is syphoned off during the process by means of a special piece of apparatus. In this way it is possible to separate 95 per cent. of the added loading materials from the rubber, and the solution obtained may be looked upon as almost pure.

For the separation of the rubber from the solvent two methods are available; it can either be precipitated by the addition of a substance—such as alcohol or acetone or a mixture of these two substances—in which it is practically insoluble; or the solvent may be driven off in a current of steam (and recovered). Very often, with a view to reducing costs, the two methods are combined, the solvent being first of all steam-distilled, whilst the last traces are separated from the rubber by the addition of a mixture of alcohol and acetone. The recovered rubber is then washed, sheeted into the form of crepe, if possible, and dried in a vacuum drier. The operation of sheeting is particularly difficult, because even after very careful distillation, precipitation with a large excess of acetone, repeated washing with alcohol, and treatment with various coagulants, such as mercuric chloride, tannin, ferric chloride, or acetic acid, the rubber remains tacky and sticks to the fingers. It has lost its nerve and its elasticity and has become greasy; even smoking has no very distinct effect upon it. This condition is due to very advanced depolymerisation, brought about by the high temperature to which it has been subjected in order to get it into solution. The rubber will sometimes recover its original characteristics if allowed to remain exposed to the air for some time, but the change is a very slow and very uncertain one.

We have obtained much the best results by subjecting the tacky rubber to the action of an acid gas, dry and cold, in a Werner-Pfleiderer mixer, the rubber being constantly masticated during the passage of the gas. Under this treatment the rubber recovers its original properties. The speed of the reaction is governed by the particular acid used, and its activity as a condensing agent. Before going any further into the study of the reclaiming process, we must draw attention to a very interesting process for the separation of sulphur, which has recently been described by Bary.[1] The originality of this process resides in the fact that the phenomenon of osmosis is brought into use in order to remove the sulphur from a solution of the vulcanised rubber in xylene.

"If a porous vessel containing a colloidal solution be immersed in a quantity of the solvent with which the solution has been prepared, the non-colloidal foreign substances in solution with the rubber traverse the porous partition by diffusion, tending to establish osmotic equilibrium. The pores of the partition must be sufficiently small to hold back the colloid, but at the same time large enough to enable diffusion to occur as rapidly as possible. It is easy to see that if a number of intercommunicating porous tubes be fixed in the vessel in which the vulcanised rubber is to be dissolved, and a slow current of the solvent be passed through them during the whole process of solution, the soluble impurities, more particularly sulphur, resins, tar, and oils, will be removed by it. Observation has shown that in the early stages of the operation the solvent leaving the circulating tubes is highly charged with dissolved material, and that it gradually becomes free from them; the operation is at an end when the solvent emerges perfectly clean."

This is obviously a very satisfactory method of separating the crystalloidal constituents of a solution of vulcanised rubber; it does away with any question of chemical action on the rubber, and, moreover, the solvent employed can be easily recovered by simple distillation. Of all the methods which have been put forward, it appears to be the most practical and the most elegant.

But, apart from this process, it will be understood that processes involving the solution of the rubber do not pay well, on account of the price of the raw material combined with the high cost of manipulation and of the materials

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[1] *Revue de Chimie pure et appliquée*, 1912, p. 269.

used in the process; and as a matter of fact the reclaiming industry is at present not over prosperous, and is little sought after. There are, however, certain types of rubber, the treatment of which is rather more profitable, and which have led to the establishment of factories in America and Germany which are to-day doing well. These are those types which are comparatively free from loading material, as, for example, grey resilient, floating, inner tubes. Practically the only added material consists of sulphur and a little magnesia, which may be disregarded in so far as it affects the reclaiming process. The chief difference between them and native products is in the degree of polymerisation, which has been affected by the heating and the mechanical working to which they have been subjected. The free sulphur is removed by a simple chemical treatment with alcoholic soda, and as the extent to which depolymerisation has taken place is less marked than in the case of the ordinary reclaimed rubbers, it is possible, to restore them, by fairly simple physical methods, to their original condition, or at any rate to a condition very similar.

Marck has succeeded very skilfully in working out a single-stage process which solves the two portions of the problem very neatly. This process consists in heating the rubber with a weak solution of caustic soda under pressure; the alkali combines with the excess of sulphur to form sulphide, thus solving the chemical aspect of the problem, whilst the heat and pressure bring about repolymerisation, and solve the physical aspect. With the reservation that it is only intended for use with slightly-loaded rubber, Marck's process solves the problem of reclamation in a very happy fashion, and wherever it has been applied it has met with complete success.

The same is true of Theilgaard's process, in which sulphites or bisulphites are employed instead of soda under conditions otherwise almost identical, or of Mitchell's process, in which sulphuric acid or sulphides are used.

Of the various "complete solution" processes, Bary's xylene process alone appears to be of interest. The above brief account is sufficient to show that the reclaimed rubber industry can scarcely be relied upon to contribute any very serious support in the task of meeting the general demand for rubber; moreover, the deterioration in most of the essential properties of the rubber which results from the reclaiming process leaves quite a second-grade product, the principal use of which is to replace vulcanised oil substitutes in mixings.

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EUCALYPTOL.

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CHAPTER IV.

COST OF PRODUCTION OF RUBBER.

The following information upon the conditions under which rubber is sold, and upon the form in which it is presented, will tend to make our account of the economic side of natural rubber more complete.

Uniformity in quality is not the rule, even amongst rubbers of the same geographical origin, and coming from the same district; the quality of such rubber may show great variations dependent, not only upon its botanical source, but also upon the conditions under which the latex has been collected, upon the age of the tree, and the time of year—even the hour of the day—when the latex was taken from the tree.

On the other hand, it will be seen that the process of coagulation may have a great influence upon the purity of the product, upon its moisture content, and upon its liability to decomposition, which latter depends upon the varying amount of putrescible substances left in it by the particular process employed.

The value of any given sort of rubber is indicated above all by its geographical origin, which gives a clue, not only to its botanical source, but also to the methods of extraction and coagulation which have been employed in its production. On the other hand, it is necessary to point out that one and the same country may produce rubbers, collected in different districts, which are by no means identical in quality; and that, on the other hand, several quite distinct qualities may come from the same region, derived from the same plants, but prepared in different ways.

The properties which are more particularly sought after in rubber are firmness, good "nerve," and a close and homogeneous texture; low-grade rubbers are generally soft, flabby, and of poor resilience. Of the lowest grades, some are greasy and sticky to the touch, whereas others are of a dry, more or less brittle character, these defects being usually due to the presence of a high proportion of resins.

It is obvious that in between these general types there are to be found all possible intermediate stages, but it is always the degree of "nerve" which serves as a criterion in judging the value of a rubber.

Commercial valuation of rubber is based upon a practical examination of a freshly cut sample taken from the bulk, and the method adopted by the expert is one of comparison, taking into account the market fluctuations.

It would obviously be better to define the quality by means of a series of chemical and physical tests designed to determine the degree of purity of the rubber as well as its strength, nerve, and elasticity. But at the present time, with the exception of an Official Testing Bureau established by the Dutch Government in Delft, under the direction of Dr. Van Herson, there is not a testing institution on any of the rubber markets.

It will be realised, from what has been said, that the price of rubber based upon its properties may vary between somewhat wide limits. In order to give a very condensed idea of this, we shall give a short account of the chief sorts now offered to the consumer, taking as the basis of our classification the three geographical groups of production.

Of American rubbers, the one which obtains the highest price on all markets on account of its purity, nerve, and uniformity is *Para,* the product of *Hevea,* collected in the Amazon basin. It is the price of Para which regulates the market price of all other grades.

As a general rule, there are three types of Para :—

1. **Fine Para,** the highest grade rubber of all, highly nervy and elastic. It arrives in the form of cakes or biscuits, weighing from 6½ to 11 lbs. in the case of the product of the Lower Amazon, and from 22 to 33 lbs. in the case of that of the Upper Amazon ; the cakes are packed in cases holding from 2½ to 3 cwts. On the outside the colour is dark brown, and when cut through the centre the cake exhibits a laminated structure, due to the method of coagulation employed ; the colour is clean, and becomes almost white towards the centre. The price of "fine Para" has risen, at certain times, as high as 12s. per lb., and its average cost in normal times has been between 5s. 6d. and 6s. 8d. per lb.

2. **Entrefine Para** is a mixed quality, with a little less nerve and containing more water than *Fine.* In outward appearance there is very little difference between the two, but the texture of Entrefine is not so highly laminated. This product is, in fact, made up of the coagulated pellicles taken from the latex-collecting vessels and from the incisions in the trees. These scraps are united to form a small lump, the size of which is then increased by immersion in latex followed by smoking ; the result of this method of procedure is that the outside portions are excellent, whereas the centre is of doubtful quality. The market value of this type of Para is uniformly about 4½d. per lb. below that of *Fine.*

3. **Sernamby,** also called **Negroheads,** is a very inferior quality made up of the scrapings and all the impurities of the collecting vessels. These scraps are heaped up and pressed into casks weighing about 4 cwts. gross. *Sernamby* is black outside, and white, veined with black, on the cut. The rubber is in the form of very irregular masses, which owe their shape to the chances of collection and compression. It is far from possessing the properties of *Fine.* Nevertheless, in virtue of its source, the market price keeps between 3s. 8d. and 4s. per lb.

There are yet other qualities of *Hevea* rubber, such as the *White Para* of Matto-Grosso, which is very similar to Brazilian *Para ;* these products, however, are less highly approved, and consequently fetch lower prices on the market.

Ceara (*Manihot*) rubber is obtained from *Manihot Glaziovii ;* it has good nerve, but is not nearly equal to Para in purity, and gives a good deal of waste. It is a more or less deep amber in colour, and comes over in the form of large blocks made up of balls or marbles, which, in their turn, are made by rolling up fine strings called scraps. The market price is about 3s. 10d. per lb. on the same basis as taken above for *Fine Para.*

Hancornia speciosa rubber or *Mangabeira* comes from the central districts of Brazil, in the form of irregular-shaped masses, or of thick slabs. In spite of the rather defective method of coagulation employed, it is a good medium sort, worth about 3s. 2d. per lb.

Castilloa rubber occurs in different forms, according to its geographical origin; either in "sheets" measuring about 20 × 24 inches and from ⅝ inch to 2 inches thick; or in "marbles," small balls 2 to 2½ inches in diameter; or in large "puddings," bulky slabs, or strings. This rubber is darker in colour than *Para*, and is also less pure, but it has remarkably good nerve. Its price varies between 2s. 2d. and 5s. 2d. per lb.

Africa furnishes a great variety of rubbers of very different kinds, of which even the best sorts are inferior to Para.

These rubbers are generally rather dark in colour—brown, reddish-brown, and sometimes slate-grey. They are prepared in the most diverse forms, such as thimbles, small cubes or dice; scraps, small balls made up of strings of rubber; discs, balls, sheets; larger masses, such as voluminous balls—frequently massed together into blocks—puddings, spindles, rectangular sheets, sheets curved or flat, large blocks, loaves, bricks, or lumps made up of irregularly shaped pieces. These various forms of the product are often packed in matting forming a kind of panier.

They are generally classified into eight grades, the first comprising sound rubbers, the others rubbers of different degrees of stickiness.

The better qualities come from Kassai, Equateur, Lopori, Mongolla, Uellé, Lomani, and Lake Leopold II., whilst the lower grades come chiefly from D'jenna, Oogoné, and the Lower Congo. Their price varies from 3s. 2d. to 3s. 7d. per lb.

From **Asia** and **Oceania** the wild rubbers generally arrive in the form of small blocks or loaves of moderate size; from Calcutta they are exported in bales covered with jute cloth and bound with cane. These rubbers are dark in colour, and generally of medium quality. The better grades are worth from 2s. 6d. to 3s. 7d. per lb. But there are also some very impure products coming from Asia, obtained by absolutely defective methods of collection, badly coagulated, putrescent, and containing only a low percentage of rubber; they are valued at a very low estimate, and are sold at a price not exceeding 9d. per lb. For some few years the London and Dutch markets have dealt in plantation rubber, obtained from cultivated *Heveas*, grown in Ceylon, the Malay Peninsula—including the Federated Malay States—Tonkin, and the Dutch Indies. This type of rubber is noteworthy on account of its great purity, but its method of coagulation, which has not yet been perfected, renders it inferior in nerve to the product of wild *Heveas*. Its price varies from 3s. 7d. to 5s. 5d. per lb.

Those types into the preparation of which a process of smoking enters have established themselves in particular favour. Coagulation by means of acetic acid, which, in spite of Wickham's efforts, still holds the field on the plantations, is accompanied by two very serious disadvantages. In the first place, the rubber is not rendered entirely aseptic, and thus tends to become tacky, and secondly, owing to the repeated washing which it has to undergo, in order to free it from acid, it becomes partially depolymerised, and loses some of its nerve.

This state of affairs will easily be remedied when the scientific methods of coagulation which Victor Henri has worked out become commonly known. Up to the year 1912 the resinous rubbers of Borneo and Pontianak were brought to Havre, Antwerp, or Rotterdam in the form of large loaves weighing 1 to 1½ cwts., and in appearance like a large white cheese; this product contained about 40 to 45 per cent. of water, 40 per cent. of various resins, and 12 to 18 per cent. of rubber, and sold for about 3½d. per lb. At present, in consequence of its contract with the Dutch Government, the concessionaire company only imports refined products with a rubber minimum of 60 per cent. into Singapore, or its other factories; such products sell at 1s. 5d. to 1s. 7½d. per lb., but there is little demand for them.

Reclaimed rubber hardly appears on the market; it is almost always sold direct by the manufacturer to the consumer at a price which is very variable and little known. Although, as will be seen, very accurate knowledge is available as to the selling value of a rubber when it arrives in Europe, it is, on the contrary, very difficult to ascertain at all exactly its cost of production in the country of origin. Although it is possible in the case of plantation rubber to form an estimate from the abundant material furnished at the annual meetings of the numerous companies, in the case of wild rubber the cost must necessarily remain in some degree hypothetical.

In fact, the expense which is attributed to the collection of the material is rather the result of the exorbitant profits taken by the local middlemen than the actual legitimate cost of collection.

In effect, for wild rubber, the value of the tree, the cost of management and of bringing the land under cultivation, all of which are expenses which reach a very high level on plantations, may be said not to exist. The outgoings scarcely include more than the wages of the collectors, the cost of lodging and feeding them, and of the purchase and depreciation of the equipment used by them, the cost of transport, and especially the commissions of the numberless intermediaries who interpose themselves between the rubber-gatherer—be he Amazonian, *seringueiro*, or African negro—and the European or American consumer.

In Brazil, for instance, the chief item in the cost consists of the sums taken by the *aviadores* both on capital advanced and on sales made. In Amazonia, where speculation has twice played havoc, it would be necessary, in order to regularise things and to get hold of the rubber at its actual cost price, to do what the Japanese tried to do in Formosa—that is to say, monopolise the industry. Several attempts have been made in this direction, and certain portions of the industry are to-day exploited either by the various States or by the Federal Government. But in order to put a stop to the time-honoured exploitation of the *seringueiro* by the *aviador*, and bring the cost of rubber down to a real figure, more energetic and forceful measures would seem to be necessary.

But even then the labour difficulty would be none the less acute, and the only remedy for this would have to be found in the introduction—highly distasteful to South Americans—of Chinese or Japanese workmen, as in the Peruvian sugar factories.

At the present time, it is estimated that, provisions being very expensive, a *seringueiro* spends about 3s. 8d. per day on his food.[1] Adding to this the cost of transport, depreciation, and renewal of apparatus, it may be taken that the workman, if he is not interested in any way, costs about 9s. 9d. per day. What is his output for this sum?

According to Chapel, an *estrada* of 100 trees, taken in an average zone, yields 36 litres of latex, or, say, 153 lbs. of Para rubber, at each tapping. Allowing one tapping per week for 20 weeks, this corresponds to a yield of 1,056 lbs. per season, for an outlay (at 9s. 9d. per day) of £68 5s. One pound of rubber, therefore, costs 1s. 3½d.

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[1] Lecointe, *Caout. et Guttapercha*, 1911, 8.

The accuracy of these figures has been contested; it has been affirmed that an *estrada* of 100 *Hevea* trees could yield as much as 1,760 lbs. per season, and that one man could produce as much as 26½ lbs. per day.

These figures were probably attained 25 years ago, in the Delta, with the trees in full growth, and with selected labour, but to-day on the upper reaches, with half-breeds or Indians, the figure of 7 lbs. of rubber per day appears to be a maximum which is rather seldom reached. Taking, then, the above cost as a basis, it is necessary to add 30 per cent. for port dues, packing, and brokerage, 5 per cent. for loss in weight, and 22 per cent. for export duty (the last being levied, not on the actual cost price, but upon an estimated value fixed by a Customs Commission). The total additions to the cost of the rubber at Belem amount, therefore, to 57 per cent., and the price becomes 2s. 0½d.; adding to this freight—32s. 6d. per ton—insurance, brokerage, selling expenses—about 3d. per lb.—the cost of the product delivered London, Havre, Antwerp, or Hamburg amounts to a little more than 2s. 3d. per lb.

At the moment manufacturers of synthetic rubber can base their calculations upon this figure; but if the State of Brazil were to remove the export duty, which brings in from £6,000,000 to £7,000,000 per annum, the price could be reduced about 5d. per lb. Finally, if it should prove possible to reduce the cost of intermediaries, and to obtain a better output from the labour employed, the lowest cost which one could hope to realise would be somewhere in the neighbourhood of 1s. 6d. per lb.

According to the *India Rubber World*, in a case where the *seringueiro* works in association with the *aviador*, the cost may be arrived at in the following way:—

The value of the rubber at Belem is assumed to be 1s. 8d. per lb., which represents the cost of running the *estradas*. The expenses per English pound, including payment of seringueiros, Federal export duty, Municipal export duty, and other charges, packing and loading, stamps, freight, insurance, total up to 4s. 2d. per lb. of rubber delivered in London; as the selling price is on the average about 5s., there is a profit of 10d.

Deducting the fictitious value, 1s. 8d., which is given to the rubber on its arrival, the actual cost price including everything appears to be 2s. 6d. per lb.

Dr. Lucien Morisse's study of the *Hevea* rubber of the Orinoco furnishes certain information as to the possible cost price of rubber in those regions so near the Amazon.

"For fine rubber," he says,[1] "the Indians are paid 1s. 3d. to 1s. 8d. per Venezuelan lb. (450 grms.), always in kind, never in cash; the broker or the contractor always makes as good a bargain as possible over the exchange. We have seen 6 or 8 lbs. of rubber demanded in exchange for knife, fork, and spoon in white metal; print or calico, worth about 2½d. per yard in Paris, was commonly sold at 1s. 8d. per *vare* (90 cm.); the price of a halfpenny ball of thread is a Venezuelan real (5d.).

If the Indian—and they are very few, there being no more than 800 Venezuelan *gommeros*—has collected a lot of rubber he has a desire for everything he sees; we have seen Hessian boots, old uniforms, an academician's robe, violins, guitars, and, above all, sewing machines bartered with him. There is not, so to speak, a hut on the Rio Negro in which there is not to be

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[1] *Lumière electrique*, 1893, 49*a*.

found a sewing machine which has cost between £40 and £50. Estimating the excess due to payment in kind at 200 per cent., this would give the cost of the rubber, delivered free at Belem, in the neighbourhood of 1s. 1d. to 1s. 3d. per lb.

It can evidently be produced much cheaper, because, according to Morisse, with intelligent labour the yields would be quite different. "We are now able," he says, "to tap on the average 912 trees, and to collect 80 litres of latex, per day." If this latex be coagulated either by the method recommended by Morisse—addition of dilute sulphuric acid and phenol—or by means of Denain's smoking apparatus, one man can produce as much as 1 cwt. of rubber per day.

Supposing we assume that these figures are exaggerated, and reduce them by one-half, for work in the tropics is very difficult, one European and three or four Indian assistants could produce as much as ½ cwt. of rubber in twenty-four hours. The cost, taking things at their worst, and making very full allowance for salaries and depreciation of plant, will not exceed 9d. per lb. on the spot, or 1s. 1½d. per lb. delivered at Belem. This figure must hold good for practically the whole of South America, where labour is scarce, communications difficult, and money dear, and where everyone's aim is to make as much as possible with the least possible effort.

In Peru the cost is a little lower. There, with Indian labour, the spot cost is 4½d. per lb., but since the only means of transport is by carriers or canoes, the cost at the ports rises to about 1s. 1½d. per lb.

In Africa it is still more difficult to reckon the cost price of wild rubber; except in Sierra Leone, in Casamance, where the rubber trees can be directly exploited, the price of the rubber depends upon the supply and demand, upon the skill with which negotiations are conducted by agents of the factories, upon the greater or less value which the negro attaches to the goods offered in payment, and lastly, upon the more or less numerous exactions to which the caravans have had to submit on the road.

These purchase prices cannot be reduced indefinitely, for below a certain figure the negro prefers not to collect rubber. At present the prices paid to the natives on the spot are approximately as follows:—

Kayes,	9d. to 1s. 1½d. per lb.
Fonta-Djalon,	9d. to 1s. 6d. ,,
Southern rivers,	1s. 6d. ,,
Gaboon,	
Madagascar,	1s. 1½d. to 1s. 3½d. per lb.

The average price, for qualities which are approved to-day, does not appear to be capable of reduction below 1s. 1½d. per lb., and that is the limit upon which it is desirable to reckon. For plantation rubber the price can be ascertained in much more definite fashion, and as it is more particularly against this that synthetic rubber will have to test its strength, it is worth while to go into the figures with all possible exactitude.

The cost includes two separate elements, which vary in different countries, but which are absolutely determinable:—

(1) The primary expenses—that is to say, cost of management and tools for the plantation.

(2) The maintenance expenses, including cost of collection and preparation of the rubber.

The following is the cost price of rubber on one of the few plantations established in the Varzea of the Amazon delta.

The plantation comprises 865 acres, which, with 200,000 *heveas*, allows of the cultivation of 230 trees to the acre. The land and laying-out of the plantation cost £17,000 ; tools, buildings, and machinery amount to £17,200 ; primary expenses may, therefore, be reckoned at £34,200, which works out at £39 10s. per acre planted. For five years this brought no return, but meanwhile maintenance expenses amounted to £20 5s., which spread over twenty years gives a charge of £1 0s. 3d. per acre per annum.

If the yield of one tapping per tree for 20 weeks be taken as 4½lbs. per tree, beginning at 6 years, the 230 trees on an acre will yield 1,035 lbs., and the labour required to obtain this will be 162 days.

Since provisioning is easy on the plantations of the delta, labour is not so expensive as it is higher up the river, and may be estimated at 6s. 6d. per day ; the cost of collection, under these conditions, will, therefore, be £52 13s. per acre.

With these data, the cost price works out as follows :—

AMAZONIA.

10 per cent. interest and depreciation on £39 10s.,	£3	19	0
Special depreciation,	1	0	3
Maintenance,	0	13	3
Labour, 162 days at 6s. 6d.,	52	13	0
15 per cent. packing, brokerage, port dues at Belem,	8	12	0
	£66	17	6

For a production of 1,035 lbs. the cost price per lb. will, therefore, be 1s. 3½d. To that must be added duty amounting to 22 per cent., calculated upon a value of the rubber estimated by the Customs Commission at 2s. 10½d. per lb. On £148 15s. 7d. the duty will be £32 14s. 7½d. The total outlay on the 1,035 lbs. of rubber when cleared from the Customs will, therefore, be £66 17s. 6d. + £32 14s. 7½d. = £99 12s. 1½d., and the total cost per lb. at Belem, including all expenses, 1s. 11d. per lb.

In Africa the creation of rubber plantations has hardly been begun, and such results as have been obtained with *Hevea* are not of a nature calculated to encourage further experiments of a similar kind. Fauchère estimates that the cost of laying down an acre in Madagascar, assuming the land to be conceded free of charge and the plants to be provided by the State, will come to about £19, whilst for the Congo Rousselot gives the figure £35 8s. ; unhappily the amount of rubber produced will hardly exceed 356 lbs. per acre, and the cost of tapping will come to nearly 11d. per lb. on account of the very poor quality of the coloured labour.

On these suppositions the cost price will be made up as follows :—

MADAGASCAR.

Interest and depreciation, 10 per cent. on £19,	£1	18	0
Maintenance,	0	13	3
Labour of tapping,	16	9	0
Packing, brokerage, port dues, 15 per cent.,	2	13	8
	£21	4	11

Or 1s. 2d. per lb.

CONGO.

Interest and depreciation, 10 per cent. on £35 8s.,	£3	10	9½
Maintenance,	0	13	3
Labour of tapping,	16	9	0
Packing, brokerage, port dues, 15 per cent.,	2	16	9
	£23	9	9½

Or 1s. 3½d. per lb.[1]

The cost works out very similar in the Indo-Oceanic regions; the statements of Bellan, the earliest planter in Indo-China, show that for 10-year-old *Heveas*, yielding 3 lbs. 5 ozs. of rubber per tree, cultivated in conjunction with coffee or tapioca, the expense of preparing the rubber does not exceed 1s. 1d.

According to Crémazy, the primary expenses in Cochin China amount to £16 9s. per acre in the Grey Earths, and £24 13s. 6d. per acre in the Red Earths. There is a tax amounting to 6d. per acre, which is only payable after seven years; labour costs 1s. 1d. to 1s. 3d. per day; Crémazy, therefore, estimates that rubber can be produced at a cost below 1s. 5¼d. per lb.

Vernet, chemist to the Pasteur Institute in Indo-China, who has visited all the Indo-Oceanic plantations, speaks from a wide experience when he says that the cost of starting a plantation amounts to about £49 7s. per acre. Wickham considers this estimate a little too high, and it may be taken that an average figure is about £32 18s. With 80 trees to the acre, a yield of 3 lbs. 5 ozs. of rubber per tree, for 130 tapping days, and allowing one man per 100 *Heveas*, the total yield will be 265 lbs., and the cost price will be made up as follows:—

Interest and depreciation, 10 per cent. on £32 18s.,	£3	5	10
Tapping, 104 days at 1s. 6d.,	7	16	0
Maintenance,	0	13	3
Packing, brokerage, port dues, 15 per cent.,	1	14	0
Imposts and taxes (after 7 years),	0	16	5
	£14	5	6

The cost price will, therefore, be 1s. 0¾d. per lb., a figure very near that given by Bellan. In the Red Earths, allowing for the labour of weeding and getting the soil into condition, the primary expenses are greater, and Vernet's figures then appear to be absolutely accurate; in this case, the yield remains the same, whilst the expenses of production of 265 lbs. amount to £15 10s. 3d., giving a cost price of 1s. 2d. per lb.

From Ceylon, the Straits, the Malay Peninsula, still more accurate information can be obtained. According to *Truth*, the cost price of rubber in Malaysia is 1s. 6d. per lb.; with this figure Torrilhon agrees; Stanley Harden gives 9d. per lb. without general expenses and depreciation, and taking primary expenses at £16 19s. 6d. per acre.

At the Plantation Rubber Congress, held at Djember (Java) in 1909, it was estimated that tapping costs in the case of *Hevea* amounted to 5d.

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[1] According to an account published by the "Compagnie forestière Sangha, *Oubanghi*," in 1912, the cost price of rubber in a district laid out in cantonments, with methodical replanting and tapping on felling, would be 2s. 0¾d. on the spot.

per lb., and that the yield from 6-year-old trees might be taken as 62 lbs. per acre, rising to a maximum of 2¼ lbs. per tree at 12 years, the cost of tapping being then 10¾d. per lb.

Mathieu, on the other hand, gives the following figures in the *India Rubber Journal*:—

A 5-year-old	*Hevea* yields	3½	ozs.	dry rubber per annum.
A 6-year-	„	7	„	„
A 7-year-	„	14	„	„
An 11-year-	„	42	„	„

Generally speaking, it is considered possible, in Ceylon, for the yield to reach from 88 to 110 lbs. per acre for 5-year-old trees, 330 lbs. for 7 to 8-year-old trees, and 440 lbs. for fully matured trees. In the Malay States it is estimated that 5 acres, in full production, are necessary to yield 1 ton of rubber, and the actual amount collected by the Selangor Rubber Company at Rengam was 66 lbs. per annum just at first with 4-year-old trees, reaching progressively 660 lbs. with 11-year-old trees. In fact, it may be taken that, according to these particulars derived from very different sources, the yield of plantation *Hevea* varies from 2¼ lbs. to 3½ lbs. per annum, whereas wild *Hevea*, according to various statements, yields in Amazonia from 6½ to 7¾ lbs. Working with the above data, and supposing the concession to have been granted free of charge, we can calculate the cost price as follows:—

INDO-OCEANIC REGION.

Primary expenses (per acre) clearing and preparing the land (Gallagher),	£7	19	3
Planting 80 *Hevea* trees,	1	12	6
Maintenance for 7 years, at £2 9s. 4d. per annum,	17	5	4
Buildings, tools, etc.,	3	15	8
	£30	12	9

Cost price of the first year's production:—

Interest and depreciation, 10 per cent. on £30 12s. 9d.,	£3	1	3½
Maintenance,	0	13	3
Tapping expenses, 5½d. per lb. on 62 lbs.,	1	8	5
Packing, brokerage, port dues, 15 per cent..	0	14	7½
	£5	17	7

The cost price is, therefore, 1s. 10¾d. per lb.

Cost price in the tenth year after planting (each tree yielding 2¼ lbs.):—

Interest and depreciation,	£3	1	3½
Maintenance,	0	13	3
Tapping expenses, 5½d. per lb on 180 lbs.,	4	2	5
Packing, brokerage, port dues, 15 per cent.,	1	2	3
	£8	19	2½

The cost price is, therefore, 1s. per lb.

The following account gives in full detail the cost of rubber on a plantation in the Federated Malay States, on the basis of 200 lbs. per acre per annum:—

GENERAL EXPENSES, PER LB.

	Cents.
Salaries,	4·73
Rents,	0·40
Visiting and agents' fees,	0·22
Interest paid,	0·43
Medical expenses,	0·80
Fire insurance,	0·17
Horses,	0·10
Labour recruiting,	0·75
Sundries,	0·57
	8·17

CULTIVATION.

	Cents.
Clearing land,	4·53
Roads, bridges, draining,	1·30
Replanting,	0·24
Wastage and deaths of trees,	0·46
Tools,	0·07
	6·60

BUILDINGS—DEPRECIATION.

	Cents.
Bungalows,	0·15
Fencing,	0·29
Factory and stores,	0·17
Machinery,	0·16
Stables,	0·06
	0·83

MANUFACTURE OF RUBBER.

	Cents.
Marking trees,	0·42
Tapping,	14·04
Attendance and fuel,	1·54
Utensils,	0·59
Packing,	1·18
Transport,	0·58
Cost of forwarding,	0·08
Customs,	4·24
	22·67

COST PER LB. ON THE PLANTATION.

	Cents.
General expenses,	8·17
Cultivation,	6·60
Buildings,	0·83
Manufacture,	22·67
	38·27 or 8¾d.

COMMERCIAL EXPENSES.

	Pence.
Freight,	6·80
Storage,	3·30
Selling expenses,	0·40
Brokerage,	2·90
Insurance,	2·30
Discount,	1·73
	17·43

Total cost in London is, therefore 2s. 2¼d. per lb.

Knowing the selling price in London of plantation rubber, it is easy to understand the huge profits made by the earlier established plantations, which are to-day in full production. In 1909 the following dividends were distributed by the companies in question :—

COMPANY.	OUTPUT.	CAPITAL.	DIVIDEND.
	Tons.		Per cent.
Linggi,	500	£100,000	87
Anglo-Malay,	500	150,000	58
Kuala Lumpur,	400	180,000	38
Selangor,	300	30,000	173
Bukit Rajah,	300	70,000	74
Vallombrosa,	300	50,000	104

In Ceylon the cost is a little lower, although it has been necessary to take and pay for exhausted tea land for creating the plantations; the primary expenses per acre are :—

Purchase,	£16	9	0
Planting,	1	12	11
Maintenance for 6 years,	14	16	1
Buildings and tools,	3	15	8
	£36	13	8

In the tenth year, for 80 *Heveas* yielding 178 lbs. of rubber, the cost will be made up as follows :—

Depreciation, 10 per cent. on £36 13s. 8d.,	£3	13	4½
Maintenance,	0	13	3
Tapping,	3	19	6
Packing, brokerage, and port dues, 15 per cent.,	1	8	2
	£9	14	3½

The total cost is, therefore, 1s. 1d. per lb.

It will, therefore, be seen that, taking a rough average, allowing a good margin for expenses and risks, and disregarding export duties, which can be taken off at any moment by Government, the cost price of natural rubber, whether wild or cultivated, is in the neighbourhood of 1s. 1d. per lb., and it is with this figure that synthetic rubber has to reckon.

The cost price of Jelutong rubber, more especially since its monopolisation by the Germans, seems as if it ought to be much higher; it is dependent upon the value which is attributed to the extracted resins. Up to the present these have only had a limited use, although the suggestion of Black and Morton to employ them—since their chemical molecule contains the divinyl group—for the preparation of isoprene, might give them a certain value. But if for the present they are priced at the same figure as very fine colophony, that probably represents the possible limit of price. On this basis the cost price of Jelutong rubber is arrived at as follows, for a 20 per cent. raw material:—

	F.	*C.*
100 kilos. Jelutong at 30 fr. per 100 kilos, ...	30	0
Petroleum ether—Loss 5 per cent. of 500 kilos—*i.e.*, 25 kilos at 35 fr. per 100 kilos, ...	8	·75
Acetone—Loss 5 per cent. of 300 kilos—*i.e.*, 15 kilos at 180 fr. per 100 kilos, ...	27	0
Ether—Loss 10 per cent. of 150 kilos—*i.e.*, 15 kilos at 100 fr. per 100 kilos, ...	15	0
Labour, ...	12	0
Drying, ...	4	0
Coal, 500 kilos at 28 fr. per ton, ...	14	0
Depreciation and interest, ...	10	0
	120	75
Resin, 40 kilos at 50 fr. per 100 kilos, ...	20	0
	100	75

Average yield of rubber, 18 kilos.
Cost price = 5 fr. 59 c. per kilo.
= 2s. 0¼d. per lb.

The cost is frequently even higher still, for Jelutong containing an average of 18 per cent. rubber is rather scarce, and it is, therefore, necessary to reckon that the cost price of Jelutong rubber is nearer 2s. 6d. than 2s.

Under these circumstances it would appear that if synthetic rubber can be produced at a cost approximating to that of plantation rubber—that is to say, at about 1s. 1d. per lb.—rubber extracted from highly resinous natural products such as Jelutong would be of no further interest. At its present cost it will only be of interest so long as the selling price of Para keeps up; if the latter should drop to 2s. or even 2s. 3d. per lb., the process of extraction would become impossible. On the basis of a price of 80 fr. per 100 kilos (3½d. per lb.), such as was asked in 1911 for crude Jelutong, the cost price of the rubber would be increased to 3s. per lb.

The same ill fortune is in store for reclaimed rubbers, especially for "completely" reclaimed types; starting with figures which we have already mentioned, the cost works out as follows:—

"COMPLETELY" RECOVERED RUBBER (BY SOLUTION PROCESS).

	F.	C.
100 kilos of pneumatic tyres,	80	0
Grinding,	6	0
Hydrochloric acid for 100 kilos at 5 fr.,	5	0
Solvent—Loss 10 per cent. of 500 kilos at 1 fr. per kilo,	50	0
Acetone—Loss 10 per cent. of 400 kilos at 1 fr. 80 c. per kilo,	72	0
Alcohol—Loss 10 per cent. of 400 kilos at 45 c. per kilo,	18	0
Hydrochloric acid gas, 20 kilos at 1 fr. 50 c.,	30	0
Drying,	4	0
Labour,	10	0
Coal, 800 kilos at 28 fr. per ton,	22	40
Interest and depreciation,	15	0
	312	0

Yield, 20 kilos of pure rubber.
Cost price = 15 fr. 60 c. per kilo.
= 5s. 10¾d. per lb.

The process is only applicable on the assumption of a great advance in the price of natural rubber, into the region of 9s. 6d. or 10s. per lb., as in 1909-10; this is on account of the cost of extraction, which is exceedingly high, because expensive materials have to be used; this item alone amounts to nearly 3s. 3d. per lb. of reclaimed product. Only more efficient recovery of the solvent and of the alcohol-acetone mixture, employed in the processes of precipitation and working, would enable the cost to be reduced, but this, on account of the high volatility of the liquids in question, would appear to be extremely difficult to attain.

Marck's process seems to be capable of giving a better result, because, although the cost of the raw material is high, the de-sulphurising agent is very cheap.

The following are the figures for Marck's process :—

RECLAIMED RUBBER (MARCK'S PROCESS).

	F.	C.
Floating inner tubes, 100 kilos,	500	0
Grinding,	6	0
Caustic soda, 25 kilos at 30 fr. per 100 kilos,	7	50
Labour,	10	0
Coal, 800 kilos at 28 fr. per ton,	22	40
Interest and depreciation,	12	0
	557	90

Yield, 85 kilos of rubber.
Cost price = 6 fr. 55 c. per kilo.
= 2s. 4¼d. per lb.

As far as one can judge, therefore, in the struggle which must eventually take place between wild rubber, cultivated rubber, and synthetic rubber, neither rubber extracted from highly resinous raw material nor reclaimed rubber—with the exception of the "Marck" type—will be able to compete, and both these classes of rubber will disappear from the market on account of their high cost of production.

SECTION II.

THE FORMATION, PHYSICAL AND CHEMICAL PROPERTIES, ANALYSIS, AND CONSTITUTION OF CRUDE RUBBER.

CHAPTER V.

THE LATICIFEROUS SYSTEM.

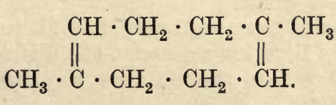
Before it is possible to realise the synthesis of an organic substance, it is necessary to have learned, by analysis, all the details of its composition. We must know not only what are its constituent elements, but also how these are grouped, and, as far as possible, how nature sets about the task of synthesis. Every synthesis must, therefore, be preceded by a complete analysis of the substance in question, and with the aid of such analysis the chemist should be able to frame a hypothesis to guide him in his work of reconstruction.

The study of a naturally occurring colloidal substance of the complexity of rubber is a very intricate business. Until within the last year or two it was hardly possible for those who had not made a special study of the chemistry of rubber, to inform themselves accurately upon the methods of investigation which had been worked out, and the theories as to its constitution which had been put forward; in other words, to acquire a compendious knowledge of what was known about the substance.

At the present time a great many obscure points have been cleared up, and all our ideas on the subject have gained something in clearness and exactness, and for this advance we are indebted more particularly to the work of Harries, Weber, Henriques, Spence, Ditmar, Kondakow, Axelrod, Alexander, Hoffmann, Perkin, Matthews, Bouasse, Bertrand, Victor Henri, Breuil, Vernet, and Jumelle.

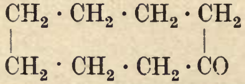
A theory as to the formation and constitution of rubber has been outlined, and we believe we know with what fundamental molecule we have to deal in this complex.

As a result of Harries' work, it is pretty generally admitted that in natural rubber, as extracted from a variety of latices and afterwards purified as completely as possible, one is dealing with a complex colloid, of very high molecular weight—Gladstone puts it at 6,000—the fundamental molecule of which appears to be one derived from an 8-carbon ring containing two double bonds—viz., dimethyl cyclo-octadiene :—



$$\begin{array}{l} \mathrm{CH\cdot CH_2\cdot CH_2\cdot C\cdot CH_3} \\ \quad\| \qquad\qquad\qquad\qquad \| \\ \mathrm{CH_3\cdot C\cdot CH_2\cdot CH_2\cdot CH.} \end{array}$$

This ring system has no known representative in nature with the exception of Willstätter's hydrocarbon and azelaone :—



and, therefore, this very special constitution can only be regarded as fully established when the substance has actually been obtained synthetically, and has been shown to be capable of polymerisation to natural rubber.

But let us admit for a moment, without reserve, the hypothesis put forward by Harries; then it is evident that dimethyl-*cyclo*-octadiene is itself derived from a less complex substance, and it seems certain that isoprene or methylbutadiene—$CH_2 : C(CH_3) \cdot CH : CH_2$—is the hydrocarbon from which it springs, as Bouchardat maintained.

On referring to Bouchardat's pioneer work, as well as to the investigations of Tilden, Harries, Hoffmann, Coutelle, Perkin, and Matthews, it will be seen that, according to the conditions under which the process is carried out, one can pass by polymerisation, from a C_5H_8 hydrocarbon, such as isoprene, either to a $C_{10}H_{16}$ terpene, like dipentene, or if not to dimethyl-*cyclo*-octadiene, the fundamental molecule of rubber, to one of its lower polymerides.

By a series of new condensations, of the number and nature of which we are still in ignorance, it should be possible to arrive at the particular complex which is identical with rubber, for the syntheses so far effected do not prove that natural rubber has been really produced.

What are the laws which control this multiple transformation in nature? What are the intermediate stages in the process? How are these compounds formed and condensed in the plant? These are so many problems which have scarcely been enunciated, and towards the solution of which it is easier to formulate hypotheses than to cite experimental facts. We shall attempt the study of these matters, but it must be said at once that all that is known about them has done very little towards bringing about the syntheses which have been achieved; these latter are, in fact, all based upon the bold idea conceived by Bouchardat of assuming a direct relationship between isoprene —which is formed in small quantity when rubber is destructively distilled— and natural rubber itself. In this study the following plan will be followed:— First of all, we shall examine the plant, and the arrangement in it of the *laticiferous vessels* in which rubber (or the substance from which rubber is formed, Weber's oily hydrocarbon) is produced; then we shall study the latex and go over the hypotheses which have been put forward to explain its formation in the plant; then we shall consider rubber properly so-called, its coagulation—an operation of the highest importance, because on it depend the technical properties and consequently the market value of the rubber— and its analysis; and finally, making use of the data acquired in the study of these points, we shall show how Harries succeeded in establishing the constitution or structure of rubber.

How do the latex, and the rubber which is its most important constituent, originate in rubber-yielding plants?

A few years ago it would have been very difficult to answer this question, for scarcely anything was then known about the histology and biochemistry of these plants. Light has been thrown upon the subject, especially in the cases of *Hevea* and *Ficus*, by the very important work carried out by Jumelle, Vernet, and Wildemann. From the botanical point of view, it is necessary, first of all, to give some information about the laticiferous systems of the different families of rubber trees, for Wildemann is right when he says that, in order to treat a rubber producer in a rational way, it is of considerable importance to devote attention to this system, and quite wrong to leave it out of account. A good deal of this information will be taken from the "Traité de botanique" of Sachs—one of the few works in which rubber has been studied from an anatomical point of view—from the works of Chauveau, Morellet, Jumelle, Pernier, La Bathie, and Wildemann; and from Vernet's studies.

The Rubber Tree and its Laticiferous System.—Rubber-yielding plants may be looked upon as the laboratory or factory in which the preparation of the product with which we are concerned—rubber—is carried out. It will, therefore, be of interest to look into their arrangement and structure, if only in a very summary fashion.

All plants are built up, ultimately, of cells of various shapes and sizes, each of which is made up of an envelope of cellulose surrounding a central cavity; these are the *utricles*. These cells, when first formed, are therefore little sacks, made up of a simple membrane, perfectly continuous and homogeneous, the substance of which is, at first, soft and moist. A second membrane is afterwards formed in juxtaposition to the first, and the thickness of the cell walls may be still further increased, as the plant grows, by the formation of several other layers in succession.

Assemblages of these cells give rise to three principal plant tissues:—

1. Cellular tissue, or *parenchyma.*
2. Fibrous tissue.
3. Vascular tissue.

In the wood, where the vascular tissue is situated, are to be found vessels known as *spiral vessels*, *false spiral vessels*, or *air vessels*, because, except when the sap is rising, they are filled with air.

The laticiferous vessels, which claim our more immediate interest, are not very often found in the inner layers; they are particularly abundant in the bark. They appear to have an origin distinct from that of the spiral vessels and the false spiral vessels. Some botanists hold that they are derived from a primordial cell; others claim that they are not, in the first instance, defined by an organic membrane at all, but that they consist simply of lacunæ left between the utricles of the adjacent tissues. Subsequently the juices circulating in this succession of empty spaces, which interlace one with the other in every direction, secrete a substance which clothes the projecting portions of the external walls of the utricles, ultimately giving rise to an envelope. This differs from the spiral tissue in being devoid of any form of spirals, dots, stripes, or rings. A result of this method of formation is that the laticiferous vessels, in a large number of plants, anastomose freely in all directions, forming a veritable net-work; this never takes place with spiral and other similar vessels.

Composition of the Wood.—Having described the composition of the plant tissues, let us consider the tree in which they are combined to form wood. In a transverse section of the stem of the tree the first point to be noted is the presence of two main portions, consisting of the concentric zones of bark and wood, separated by a thin growing layer, the *cambium*. The elementary tissues forming these divisions may be grouped as follows :—

- BARK, . .
  - Epidermis,
    - Cuticle.
    - Dermis.
  - Corky envelope.
  - Green parenchyma or nutritive cortical tissue.
  - Liber,
    - Cortical fibres.
    - **Laticiferous vessels.**
- CAMBIUM, or growing tissue.
- WOOD, . .
  - Fibro-vascular tissue.
  - False spiral vessels.
  - Spiral vessels forming the medullary sheath.
  - Pith, or medullary parenchyma, or nutritive tissue.

The green parenchyma, or nutritive cortical tissue, contains the chlorophyll; in rubber-yielding trees the laticiferous vessels which are present in the tissue are filled with saccharine and gummy substances, the parenchyma constituting, in a sense, the pith of the bark layer.

Each year a layer of bark and a layer of wood are formed; the zones of bark being continuously forced outwards to the periphery, the epidermis becomes distended and begins to scale off. The laticiferous channels, during this process of distension, are apt to be damaged, and the juices which they contain to be distributed throughout the wood, or to be driven to the exterior of the tree. Such an occurrence rarely happens in the case of rubber plants, with the exception of *Guayule*, but is common amongst pine, fir, and larch. If the bark also loses its corky envelope and its parenchyma, nothing remains of it but the liber, to which a fresh layer is added every year, next to the cambium, and very rich in laticiferous vessels. It appears to be the cambium in which the descending sap lingers for a certain time, whilst the materials which are to be taken up by the laticiferous channels are being modified. The physiological rôle of this tissue is a considerable one.

The pith, or nutritive cellular tissue, has its utricles gorged with juices; it is united with the parenchyma through the medullary rays, which serve as connecting links between the two nutritive tissues, and so render possible the interchange of alimentary materials or of transformed or waste products.

The laticiferous vessels are generally most numerous in the bark, either in the green parenchyma or in the liber.[1] These channels take the form of cylindrical cavities, lined with a special membrane, formed of very small cells. These cells appear to possess the faculty of extracting from the sap, by some little understood mechanism, the elements of rubber, and of accumulating them in the laticiferous vessels, which are arranged longitudinally with respect to the fibres, and transversely to the direction of the medullary rays. The vessels are not very numerous in the spring wood, but are very abundant in that of autumn.

Knowledge of the arrangement of the vessels affords an explanation of the fact that, in trees yielding latex, when the bark is damaged they are torn open and allow the rubbery liquid to flow out through the wound, either to coagulate in the form of hemispherical masses on the spot, or to run down the trunk of the tree in threads.

The Laticiferous Vessels.—In most secreting plants, before a wound has

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[1] Otto Chimauri has found a large number of trichomes, full of globules of latex, in the epidermis of *Castilloa*.

been made only a limited number of main *laticiferous vessels* is to be found; on wounding them, secondary vessels are formed, and the flow of latex is at once physiological and pathological. Such is the theory of tapping which Tschirsch has established as a result of his investigations on the conifers, and although analogous work has not been done on rubber plants, they may be regarded as following, in most instances, this general law. Moreover, Vernet's work will throw much light upon this point.

As there are several hundred species of rubber trees extant, it is obviously impossible to examine each species botanically in such a way as to describe the peculiarities of the laticiferous vessels; the majority of them have not been investigated. One is compelled, therefore, to limit one's attention to such general characteristics as have been brought out by the examination of some of the better known species, such as *hevea*, *manihot*, *ficus*, and *castilloa*. The vegetable mechanism must be practically the same in all cases, and the organs of secretion and transformation cannot vary much.

The following data have been derived from a comparison of the various publications on the laticiferous vessels of rubber plants :—

The idea that the latex must be contained in specialised cells was first put forward by Malpighi, in 1675, in his *Anatomia plantarum*. In 1812, Molden Hawer described the formation of the laticiferous vessels, regarding them as derived from an initial cell; this theory was confirmed by Unger, who showed that not only did the primitive cells become elongated, but their transverse walls underwent absorption where they happened to be in contact. The formation of the vessels is, therefore, the result of a process of fusion, coupled with the disappearance of the transverse partitions.

In 1877, Schmalhausen endeavoured to show that these vessels were not articulated, but that they were derived from initial cells pre-existing in the embryo and increasing in size with the tissues of the plant.

Chauveaud's work, completing that of Schmalhausen, definitely settled the constitution of the laticiferous systems of the principal families of rubber plants, and latex-yielding plants were classified into three main categories :—

(1) *Articulated Vessels.*—Euphorbiaceæ (*Hevea, manihot*); Compositæ, Chichoreæ, Campanulaceæ.

(2) *Non-articulated Vessels.*—Euphorbiaceæ (except *Hevea* and *manihot*), Moraceæ (*ficus* and *castilloa*), Apocynaceæ (*funtumia*), Asclepiadaceæ.

(3) *Solitary or Articulated Cells.*—Sapotaceæ (guttapercha).

Rubber may also occur in certain special cells, non-anastomosed, as in the *Wimmerins*, where it is present, in the form of small masses, in the parenchymatous cells.

It was found by Loesener in the bark, leaves, and even the inflorescences of *Gymnosporia*. It is now regarded as demonstrated that the various systems of laticiferous vessels may be found, in different individuals, amongst latex-yielding plants, first of all in the bark of the stems and branches, then in that of the roots, and lastly, but more seldom, in the inner layers of the wood, in the pith, in the leaves, flowers, and fruits.

Generally speaking, it is in the stem and the root that the vessels are the most fully developed and the richest. Under normal conditions, the latex is in particular evidence in the stem, and it more especially abounds in the vessels of the bark.

At the inter-nodes the vessels appear to be almost isolated, forming long cylindrical tubes with a very occasional lateral branch, which may form a channel of intercommunication between them.

At the nodes there are formed ramifications, which anastomose into a network forming small, fine prolongations, which end in blind, finger-shaped tubes.

In certain leaves, such as those of the figs, the vessels extend well into the parenchyma, reaching so far as to make direct contact with the epidermis.

In the Asclepiadaceæ and Apocynaceæ, the vessels bear a great resemblance to the fibrous elements of the liber, from which they can often only be distinguished by the presence of the latex. In the case of these families it is to be noted that the thicker the consistency of the vessel-contents the thinner are their walls, a fact which would seem to indicate that, in accordance with Weber's ideas, the cellulose of the cell envelope plays a certain part as raw material for the production of the rubber. In the rhizomes, the vessels are situated in the outer cortical layers; their walls are thin and the latex in them very thick. In the *Vaheas*, the arrangement of the vessels is different; one finds first of all several layers of parenchyma alternating with layers of liber, and then, beneath the innermost layer of this tissue, one comes across the laticiferous vessels, in close proximity to certain resiniferous canals, filled with a red resin, of high colouring power.[1] This arrangement is reproduced in many rubber trees, and it is easy to see that when the trees are tapped both networks of vessels are wounded, and rubber and resin exude simultaneously, mixing together as they flow from the wounds. Weber states that the resin canals are more abundant in the branches than in the trunks of the trees.

In other kinds of trees, such as *Callotropis*, there are tannin cells adjacent to the laticiferous vessels.

There are still other peculiarities to be mentioned. In *Kickxia*, for example, the medullary vessels contain as much latex as the laticiferous vessels; in *Urceola elastica* these vessels occur in a mass in the liber, and the green parenchyma does not contain any.

The vessels of the *Euphorbiaceæ* have the thickest walls of any, and their transverse section resembles that of the fibres of the liber. This greater thickness evidently corresponds with a greater richness in secretory protoplasm, and explains the productive power of *Hevea*. In this family the laticiferous vessels reach their fullest development in the neighbourhood of the bundles in the liber; from this point they send forth branches into the bark, and sometimes even up to the pith, through the fibro-vascular bundles. They form, in particular, numerous ramifications at the nodes of the stem, and at the bases of the leaves.

In the case of *Hevea*, the most important individual amongst rubber-bearers, the vessels are, as already stated, articulated; they are found, not only in the roots, stems, and leaves, but even in the flowers and fruits. They are derived from a series of cells, which are in the first place isolated, and make irregular contact with one another in the tissues. The transverse walls become absorbed, forming tubes arranged more or less longitudinally. The study of this system of vessels has shown that the separating partitions of these initial cells, the union of which forms the vessel, are not always completely broken down, and the persistence of a certain number of these fragments of cellular membranes might be one of the causes of variation in the yield of latex from *Hevea* trees.[2]

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[1] Morellet, *Caoutchouc, Origine botanique, Procédés de récolte*, Paris, 1884.

[2] Wildemann, *Caoutchouc et Guttapercha*, 1909, 6, 1190.

Unfortunately it is not yet known what determines the disappearance of this cell wall. If it be true that the complete suppression of the transverse walls has an influence upon the flow of the latex, investigation ought to be made to discover a means of facilitating and accelerating the disappearance of these partitions.

Scott has shown that, in the embryo plant, well-developed laticiferous vessels are already in existence, forming a complex, highly anastomosed system. Whilst the transverse partitions of the cells are becoming perforated and then absorbed, other perforations are forming in the lateral walls, setting up communication between the cells of the living tissue and the vessels. The laticiferous system does not seem to remain continually its own master, and it is being incessantly modified. New cells appear in the young bark, to the detriment of those cells which are derived from the cambium zone, the function of which is to supply, not only the tissue for the healing-up of wounds, but also the laticiferous zones.

The longer the bark remains on the tree, the greater will be the number of the fused laticiferous cells, and the greater the development of the latex vessels, which can hardly increase in size, except by the fusion of cells—that is to say, by the disappearance of the partitions of the two elements coming into contact.

On the subject of the histology of *Hevea*, Vernet has published a masterly study, which is perhaps the most complete work on the subject extant. We feel compelled to reproduce it, almost in its entirety, for it constitutes a document as rare as it is valuable.[1]

" On examining the trunk of a *Hevea* tree, there is found on its surface a grey or brown layer, generally cracked and fissured, which is, botanically, dead epidermis, scaling off in places. On removing this layer a thin stratum of a yellow colour is exposed; this constitutes the corky peridermis of the plant. This protective cork is formed of one or two rows of cells with walls thickened in the direction of the periphery. Next, a tender, fairly thick, green layer is met with, the colour of which becomes less distinct in tone in the deeper portions. On examining this tissue under the microscope, it is seen to represent the external cortical layer, and to be made up of cells with clearly visible chloroleucites. Certain sclerose patches are also to be observed in places, distributed through the cortical parenchyma, and particularly abundant in the inner layers. Below this there is a highly granular space, on the surface of which a few tiny droplets of latex may sometimes be seen, though always at comparatively wide intervals. Under the microscope a cortical parenchyma is seen in this position, the cells of which contain elliptical starch grains, the major axis of which measures from 3 to 10 mm.

" In the midst of this parenchyma are some isolated laticiferous vessels, and numerous sclerose masses, which confer on the true bark its granular character.

" If the liber, which lies just beneath the true bark, be wounded by any means whatever, the latex is seen to make its appearance; if a deeper cut be made it will be found that in the lower layers the same phenomenon does not occur; the liber is then the only part of the tree which contains latex.

" To the naked eye the liber appears as a felted mass of short fibres,

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[1] *Caoutchouc et Guttapercha*, 1909, 6, 3531.

running generally in a vertical direction. Microscopic examination of the tissue brings out points of great interest. In transverse section, in the neighbourhood of the bark, there will be noticed some sclerose patches which do not appear in the deeper parts. In lateral longitudinal section, they are again found near the bark; then come parallel rows of cells, which seem to have been added one to the other, end to end, in a vertical direction; and, lastly, canals containing latex, and appearing to run parallel with the above rows of cells, are seen. These tubes anastomose with one another, at rare intervals, in a transverse direction.

"An accurate idea of the anatomical composition of the liber may be obtained from an examination of an anterior longitudinal section; it will then be seen that the laticiferous vessels and the rows of cells which have been spoken of, are neither rectilinear nor parallel, but that they form a kind of network, through the meshes of which pass the medullary rays. Numerous instances of anastomosis between the ends of the laticiferous tubes, which are nearest one another, will also be made out, and it will be noticed that the wavy walls of these tubes exhibit considerable variations in thickness. There are, therefore, some striking analogies between these vessels and the sieve tubes, but the sieve tubes, according to Van Tieghem, constitute a tissue devoted essentially to transport, conveying the nutritive materials for the plant. In a transverse direction the anastomosing branches of the latex tubes are insignificant, but concentrically with the trunk they are very numerous, the result of this being much easier communication between the vessels laterally than in the direction of bark thickness.

"The *cambium*, which is situated below the liber, is a growing tissue, the function of which as a repairing agent has already been referred to. The total thickness of the layer of bark and liber may vary, according to the age of the tree, from 1 mm. on the branch to 10 to 15 mm. on the adult trunk, the thickness of the liber itself being 4 mm.

"The whole of this consequently forms a tissue functioning essentially as a conveyor of materials, and it may be interesting to know the direction of the current of latex which traverses the interior.

"There are two determining causes: one, of a general nature, due to the evaporation of water from the leaves; the other peculiar to the particular plant.

"The laticiferous vessels being swollen with liquid, the adjacent cells exert upon them a pressure determined by the turgescence of their *hydroleucites* and the imbibition of their membranes. This is the cause, moreover, of the exudation of latex when the tree is wounded. As there is a difference of pressure between the lower and the upper parts of the stem, as well as a difference in the rate of coagulation at the base and at the summit, two currents in opposite directions may be produced. These are the more rapid as the soil is moister, the leafage thicker, and the atmospheric temperature higher."

Dr. Pedro Arens[1] has studied the laticiferous systems of *Manihot* and *Hevea*, and has arrived at the conclusion that they are almost identical.

In the young *Manihot* there are three systems of latex vessels; the first is situated in the primary bark, the second is between the pericle and the cambium zone, the third in the pith.

Of these three systems, the second alone is of importance, for, when the

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[1] *Gummi Zeit.*, 1911.

trees reach a certain age, the vessels in the outer bark disappear, and those in the pith become very scarce.

On the other hand, a large number of cells, formed, on the cortical side, by the division of the cambium cells, become transformed into latex tubes, and it is only here that new latex vessels can be formed; and, naturally, since they can only be produced when cambium cells are present, it is absolutely necessary to preserve the latter intact when the tree is being tapped; a similar observation has already been made by Wildemann.

Both in *Hevea* and in *Manihot* the latex vessels are characterised by vigorous anastomosing branches, as already explained, and it is these which, furnishing as they do communication between vessel and vessel, insure the continuous production of latex during tapping, the whole system having an outlet at the points where the tree is tapped.

It is this which differentiates these two rubber trees very sharply from *Ficus*, in which, as will be explained, the latex vessels are not anastomosed, but form true closed cavities.

From another viewpoint the anastomosis of the latex vessels affords an explanation of the rapid exhaustion of the tree which follows upon tapping too frequently, or over a surface not in proportion to its power of secretion. A falling rubber content and an increase in the proportion of serum in the latex are very sure indications that tapping has been badly carried out. In such a case there is only one thing to be done—namely, to give the tree a complete rest, and allow its wounds to cicatrise. Vernet[1] has studied *Ficus elastica* from the histological point of view, and in his excellent work are to be found some items of information which it may be well to mention. In *Ficus* latex vessels are to be found in small numbers in the epidermis, in larger numbers in the bark, but mostly in the liber. Under the microscope this uneven distribution is readily made out.

The dimensions of the vessels vary, according to the layer in which they are situated, from 5 μ to 12 μ in the bark to 20 μ to 80 μ in the liber. They are parallel with one another, and in longitudinal section show no signs of anastomosis; this arrangement explains why the flow of latex, which is very abundant when tapping takes place, very quickly ceases; the vessels having no means of communication with one another, the production of latex can only take place in the neighbourhood of the incision. In the liber, the latex vessels are thrown together in the middle of fibrous bundles which are extremely resistant, and under these circumstances spontaneous cicatrisation cannot take place; a knob of parenchymatous tissue is formed, and it is necessary to wait a very long time for new vessels to form in the reconstituted liber. These peculiar histological conditions tend to destroy the interest of *Ficus* as a rubber producer.

In *Guayule*, Cross[2] has found that the rubber is produced throughout the plant; it is found in the cells of the pith, in the medullary rays and the cortex, in the wood, and in the leaves.

In rubber plants with rhizomes, like *Ekanda*, the latex vessels are distributed throughout the racine.

Lastly, in the *lianas*, according to Father Merlon, two kinds of vessel are met with; one kind is capable of yielding a first-class rubber, whilst the

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[1] *Caoutchouc et Guttapercha*, 1909, 6, 2663.

[2] *Caoutchouc et Guttapercha*, 1909, 6, 2384.

other furnishes only an acid latex, which forms a tacky product on coagulation.[1]

Having gained an acquaintance with the anatomy and the situation of the organs secreting rubber in the various kinds of rubber plants, we will endeavour to explain by what mysterious chemical process the plant transforms into rubber the elements with which it is provided by nature.

Formation of Rubber in the Plant—Hoffmann's Theory.—Very little is known of the mechanism of rubber-formation in various plants; no work has been published on the secretion of latex comparable with that of Mayer or of Nottberg on turpentine, or with that of Charabot or de Hesse on the essential oils.

Dr. Hoffmann, one of the inventors of the German synthesis, gave a very simple explanation of the formation of rubber in the plant, before a meeting of the Association of German Chemists held at Fribourg in May, 1912. He assumed that butadienes were first formed in the rubber plants, and that these compounds were polymerised under the influence of tropical sunlight, in presence of certain unknown catalytic substances existing in the cells of the living plants. This hypothesis has as much probability as many others, and it is extremely tempting to suppose that the plant has only to form butadienes of simple constitution, and that these will immediately condense, at will and in accordance with the necessities of the case, to form terpenes, resins, rubber, etc. As for the butadienes themselves, we are quite in the dark as to their mode of formation.

Is ordinary butadiene formed in the first instance, and then methylated by means of formaldehyde, under reducing conditions? This problem has not been solved. Nature puts two materials at the disposal of the plant; how does the rubber plant form butadiene starting from water and carbon dioxide? On this subject Hoffmann maintained a discreet silence; and he was quite right, for to this day no work has been undertaken in connection with this hypothesis of formation; it is very much to be regretted that this problem in vegetable biochemistry has not been cleared up.

Transformation of Carbon Dioxide and Water Vapour by the Plant.—The data of the problem are the following:—Nature supplies water and carbon dioxide, waste products of animal life; how are these inorganic compounds transformed in the plant into organic matter? As regards the formation of the glucosides, the sugars, and even of cellulose, the problem has been partially elucidated, but beyond that only more or less likely hypotheses can be put forward. Rubber is not formed directly from water and carbon dioxide, but indirectly, either through the terpenes or terpene alcohols which Alexander has found in certain latices; or through cellulose as suggested by Weber; or, more probably still, through the starches or sugars, of which numerous traces are found in serums; this is the view supported by Harries, who regards the terpenes and rubber as derived from pentoses.

We will take this first phase of the process of formation, and endeavour to summarise the known facts.

Green plants possess the valuable power of being able to lay hold of the carbon dioxide and water vapour in the atmosphere and convert them, by

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[1] In the Venezuelan plant, the Tiñas—a species of liana which is very abundant—the rubber is present exclusively in the seed, which resembles a coffee bean in form. It contains about 78 per cent. of rubber and 12 per cent. of resins.

a synthetic process, into the carbohydrates of which their tissues are built up. They are in a sense, says Daniel Berthelot, machines for raising chemical potential, working under the influence of light. The only function of the latter consists, as it has been neatly put by Lemoine, in lowering the temperature at which, under normal conditions, these chemical reactions will take place, or, at any rate, in accelerating them.

Much as the part played by chlorophyll in these changes has been discussed, it must be regarded as the catalyst which lowers the chemical potential of reactions. Chlorophyll it is which enables vegetable tissues to bring about, with the aid of visible radiation, especially the red and orange, reactions which under the influence of light alone—photolysis—are only possible with the ultra-violet—that is to say, with radiation of high frequency. This function of catalysts which evidences itself here, in photolytic reactions, is well known in chemical reactions.

However important, of its kind, may be the action of these catalysts, the intensity of lighting still remains the principal factor. This explains why, in order to produce a substance so complex as rubber, which requires a great expenditure of energy, the cultivation of the producing trees can only be carried on successfully in the tropics, where the character of the sunlight is peculiar.

It is no part of our present plan to consider how the chlorophyll cells are formed, and what is their physical and chemical constitution; that would carry us too far, and on that subject we must refer the reader to the work of Armand Gautier and others.

Let us be content with seeing how these cells carry out their work. How does light affect them? What portions of the solar spectrum are absorbed by them, to play a part in their chemical changes? How is the absorption of carbon dioxide and water effected? Through what different stages do these compounds pass within the plant prior to their ultimate conversion into rubber? And what expenditure of energy does such a process represent? These questions form a series, the answers to which, furnished by the work of a number of scientific men, we shall endeavour to summarise.

Since modern chemistry has shown that a number of the phenomena displayed by living organisms are identical with those exhibited by non-living matter, attempts have been made to bring the physiological phenomena of anabolism and katabolism under the same physico-chemical laws as regulate the behaviour of inanimate materials.

Thus on the subject of the assimilation of carbon dioxide by plants, a series of hypotheses have made their appearance at different times seeking to explain, by means of chemical reactions, the reduction of carbon dioxide and the accumulation in the plant of products having a high chemical potential.

Action of Light and Chlorophyll.—In his book on *Colour and Assimilation*, Engelmann has made the following statements, which it will be as well to quote:—

"Chlorophyll is the active agent in the decomposition of carbon dioxide, which cannot be brought about by colourless protoplasm.

"In green plants, the absolute maximum of assimilation is brought about by the red rays, between lines B and C of the spectrum; this corresponds with the first and most prominent absorption band in the spectrum of chlorophyll. The extreme red, which is only slightly absorbed, has not much effect.

"The minimum occurs in the green, between lines E and C, and coincides with minimum absorption.

"There is a second maximum in the blue, in the neighbourhood of the F line, towards the extreme right of the spectrum.

"The maximum energy coincides, in the case of chlorophyll with maximum absorption—that is, in the red."

According to Herchefinkel,[1] the ultra-violet rays have a like action, and the later experiments of Daniel Berthelot and Gaudechon have shown that this view is well founded. In passing, it would be interesting to know what is the action of radio-activity on chlorophyll; the preliminary investigations of Kling and Herbert indicate that it is similar to that of light.

Having dealt with the physiological and physical action of chlorophyll on carbon dioxide and water, we may now consider the chemical side of the reaction, and see what changes these compounds undergo within the plant subsequent to absorption.

It is known that if a living green leaf be placed in an atmosphere of carbon dioxide and water vapour, and exposed to solar radiation, a stick of phosphorus placed in the same atmosphere will begin to give off fumes of phosphoric acid, showing that oxygen has been liberated.

The apparent change which has occurred is, therefore, represented by the equation

$$CO_2 + H_2O = O_2 + H \cdot CHO$$

in accordance with the principles put forward by Boeyer, who sees in formaldehyde the first step in vegetable transformations. The reaction which actually takes place is really more complex.

It is quite possible that only a partial reduction is effected by the chlorophyll, the carbon dioxide being reduced to carbonic oxide, according to the equation

$$CO_2 = CO + \tfrac{1}{2}O_2.$$

If that be the case, one volume of carbon dioxide should yield one volume of carbonic oxide, and half a volume of oxygen; but experiment has shown that for each volume of carbon dioxide one volume of oxygen is obtained.

Some other substance must, therefore, be decomposed at the same time, and this substance can only be water; we arrive, therefore, at a second phase, represented by

$$H_2O = H_2 + \tfrac{1}{2}O_2.$$

Thus carbon dioxide and water, decomposed by chlorophyll, yield two gases, carbonic oxide and hydrogen; how do these two gases behave in contact with one another? The study of the compounds formed by them under different conditions, and especially under the influence of the silent discharge, which is comparable with that of light, has been carried out by various workers, and the results obtained may give us some information.

Brodie found that methane is formed, according to the equation

$$2CO + 2H_2 = CO_2 + CH_4;$$

and Thénard obtained formaldehyde on subjecting a mixture of hydrogen and carbon dioxide to the action of the discharge.

The results of these experiments lead to the following conclusion:—That

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[1] *Comptes rendus*, 1909.

carbon dioxide and water interact, forming carbonic oxide, hydrogen, and oxygen; carbonic oxide and hydrogen interact giving methane, which is itself transformed into water and formaldehyde.

All this would clearly be very hypothetical were not certain experimental facts available which lend some support to this speculative theory.

Reincke, for instance, has shown that the reducing substance which can be extracted from vine leaves is no other than formaldehyde, or its polymeride, trioxymethylene.

Kumpfein, and afterwards Pollachi, arrived at the same conclusion after careful experiments.

The principle enunciated by Boeyer—viz., that formaldehyde is the first product of the assimilation of carbon dioxide by the plant—may, therefore, be regarded as demonstrated.

But is the process of formation as simple as has just been indicated?

Bach's Theory.—To this query Bach returned a decided negative. According to this Genevan scientist, carbon dioxide does not take part in chemical reactions as the anhydride, CO_2, but as the hydrate, $CO(OH)_2$.

The distinction between the system $[CO_2 + H_2O]$ and the hydroxy compound $CO(OH)_2$ carries some very important consequences from the point of view of our present problem. In the vegetable organism when large numbers of substances of very complex nature are present in contact with one another, intermediate reactions must play a decisive part; it is in part owing to these intermediate products that plants are able to realise, at ordinary temperature, syntheses which we are powerless to reproduce.

We assumed, just now, that carbon dioxide decomposed into carbonic oxide and oxygen; but, as a matter of fact, only a single class of substances, capable of yielding oxygen in the cold, is known. These are the peroxides. Therefore, to enable carbon dioxide to decompose, in the green parts of the plant, yielding oxygen, an unstable peroxidised product must be formed, either directly or indirectly, as an intermediate product.

According to Bach, the equation should be written—

$$3(CO_3H_2) = 2(CO_4H_2) + \underset{\text{Formaldehyde.}}{\boxed{C + H_2O.}}$$

The compound CO_4H_2 is percarbonic acid—derived from percarbonic anhydride, CO_3, a known substance—which, under the influence of the oxidases contained in the plant, decomposes at ordinary temperatures into carbon dioxide, water, and oxygen, hydrogen peroxide being formed as an intermediate product.

The reaction may be written—

$$\begin{aligned} 2(CO_4H_2) &= 2CO_2 + 2H_2O_2 \\ &= 2CO_2 + 2H_2O + O_2. \end{aligned}$$

On combining these two equations, it will be seen that of three molecules of hydrated carbonic anhydride which take part in the reaction, two undergo a kind of intramolecular oxidation at the expense of two oxygen atoms of the third, which is thus reduced to formaldehyde. The two molecules of percarbonic acid, which are thus formed, then decompose, each of them losing an atom of oxygen yielding again carbon dioxide, which re-enters the cycle of reactions.

Bach's theory receives support from the fact that in 1878 Clermont[1] pointed out the presence in plants of hydrogen peroxide, or analogous compounds, an observation which was afterwards confirmed by Wurster.[2]

Bach has, moreover, by means of very accurate and extensive experiments, demonstrated incontrovertibly the presence of hydrogen peroxide in insolated green plants. Hydrogen peroxide reacts with formaldehyde yielding formic acid, the presence of which in the serum of latex has been determined by Rathje.

On the other hand, formaldehyde reacts with the products which arise from the reduction of nitrates by the plant and forms hydroxylamine, which is reduced to formamide by formic acid. But the transformation of carbon dioxide and water does not stop short with the production of formaldehyde.

Tollens, and later Fitschenko, observed that formaldehyde was converted into methyl alcohol under certain circumstances, notably in presence of magnesia, which is found in latex. Delépine found that this conversion could also take place under the influence of water, formic acid being produced at the same time, according to the equation—

$$2H \cdot CHO + H_2O = CH_3 \cdot OH + H \cdot COOH.$$

In addition to the changes referred to above, formaldehyde is, of course, susceptible of many others, and in particular, is capable of undergoing polymerisation.

Formation of Fructose.—Polymerisation results in the formation of a sugar, as was demonstrated by Butlerow; the work of Tollens, Loew, and Fischer has also confirmed the existence of a fructose, the formation of which Liebig was the first to predict. Pokorny, Hugo von Mohl, Stahl, and Morgan also found that, in plants, not only was formaldehyde converted into fructose, but that it also yielded starchy substances.

In brief, as our knowledge stands at the moment, we are justified in supposing that all the carbohydrates found in the plant may be formed, by means of successive polymerisations, condensations, and reductions, from carbon dioxide and water, through the intervention of chlorophyll and under the influence of the solar rays.

A large number of the carbohydrates pass into solution in the sap; the entry of water by the roots and its evaporation from the leaves bring about a continuous circulation, the rapidity of the current increasing with the moistness of the soil and with the temperature.[3]

In this journey through the plant, the compounds originally formed may undergo a thousand and one modifications, under the influence of diastases, which split them, oxidases which bring about their oxidation, catalysts which modify them, polymerising them to larger, more highly condensed molecules, and precipitating them; whilst in presence of the utricular tissues the colloids are sorted out from the crystalloids by osmotic action.

The chain of processes by which, and the conditions under which, such changes are brought about constitute at present a close secret of nature, which achieves the greatest results by the least imposing means.

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[1] *Ann. Pharm. Chim.*, 1878, 5, 17.

[2] *Comptes rendus*, 1888, 1525.

[3] To ensure a good yield of latex, rubber requires a temperature between +26° C, and +42° C. and an annual average rainfall of at least 78 inches. *Landolphia owariensis*, which, on the authority of Chevalier, gives good yields of rubber in the tropics, does not yield latex when grown in Europe. (Wildemann.)

By making use of the enzymes, catalysts which, like chlorophyll, weaken passive resistance, the plant, with low potentials, with low frequency radiation such as that of the orange and red, with the aid of special forces like that of capillarity, realises with ease the synthesis of carbohydrates, and quaternary compounds which the use of the ultra-violet rays has enabled us to obtain at ordinary temperatures. It is with reason that Charabot regards the plant as the most marvellous laboratory in the universe.

Having considered these fundamental points, let us see how rubber may possibly be formed, starting with materials of which we have been able to discover the mode of formation.

Referring to the analyses of latex given further on, and more especially to the work of Aimé Girard, one is struck by the presence, in most serums, of sugary substances, or of ethers derived from them, or, again, of starch.

Is Rubber derived from the Sugars?—It is known that from erythritol it is easily possible by the action of formic acid to derive erythrene or butadiene, from the methyl derivatives of which Hoffmann supposes the rubber in the plant to be formed.

It is, therefore, legitimate to suppose that, by some chemical process to which we do not yet possess the key, either starch or sugar,[1] or even cellulose, is, under the influence of enzymes as yet unknown, transformed into erythritol.

The sap, rich in formic acid, produced by the oxidation of formaldehyde, would interact with these carbohydrates, converting them into butadiene.

This explanation is evidently too simple, and things cannot go on in such an elementary fashion; the intermediate products, which are always found in great numbers in the simplest biochemical operations, must play a very important part in this series of transformations, but, unfortunately, to this day none of them have been definitely isolated, except perhaps *viscine.*

That is due to the fact that no complete analysis of a living rubber plant has been made. Alexander has certainly made some little study of *Guayule,* and Vernet has made some researches on *Hevea,* but no work comparable with that of Nägeli, Trécul, Jacquemin, or Aimé Girard on the potato has been carried out.

All that is known is that latex-yielding trees all contain, in addition to rubber, starch and methylinositol or its ethers, as has been shown by Girard, de Jong, Pickles, and Whitfield, whose researches have already been mentioned.

Cross has noted, again, that the roots of *Manihot Glaziovii* are covered with tubercles, rich in latex and in starch.[2] These are, to begin with, soft and spongy when the tree is young, but as it grows they become elongated, lose their contents, and end by becoming merged in the root when the tree has arrived at full maturity. This would seem to indicate that the materials which have accumulated in this part of the plant are reserve materials, and that, therefore, the latex is by no means a waste product of physiological activity. We shall return to this important point.

Nothing is more natural than to find starch in the *Manihot,* for many trees of this family—the *Jatropha* and *Manihot utilissima,* for example—

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[1] Bourquelot and Herrissey have found that in the essential oil of the *Herb Bennet* (*Geum urbanum*) the *eugenol* is derived from a glucoside, under the influence of an *enzyme;* the glucoside is formed in the green parts of the plant where it comes into immediate contact with the diastase by which it is modified.

[2] *India Rubber Journal,* 1882, 1, No. 89.

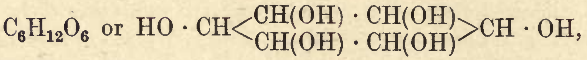
yield starchy material in abundance, from which Cassava and Tapioca are prepared. Other rubber plants, like the Artocarpeæ, are equally well provided with starch, and it is partly this richness which has earned them the common name of "Bread tree."

According to Bleicher,[1] the latex of the *Euphorbiaceæ* also contains starch, which Sachs describes as taking the form of long rods thickened at the ends. It is also sometimes found in the form of spindles. Hertig and Dippel, studying *Euphorbia splendens*, have made a similar observation, and Briosi holds that the underground stems of the plant form its natural reservoir, from which the sap current carries it into the latex vessels of the liber, where it is deposited.

In rubber plants with rhizomes the starchy material is still more abundant, and it may be noted that Gaboon rubber, from which Dambonite was first extracted, is obtained from such plants.

Whether it be in the form of inositol, methylinositol, or dimethylinositol, as extracted by de Jong from the latex of the Sumatra "Melabocai," a sugar always appears to be present in the serum of rubber latex, and it appears to be a transformation product of starch, produced by the action of a particular diastase.

Moreover, the passage from starch or cellulose, $(C_6H_{10}O_5)_n$, to dambose (inositol)



$$C_6H_{12}O_6 \text{ or } HO\cdot CH{<}\begin{matrix}CH(OH)\cdot CH(OH)\\ CH(OH)\cdot CH(OH)\end{matrix}{>}CH\cdot OH,$$

is fairly easily explained.

On the other hand, it is known that erythrene can be obtained from erythritol by the action of formic acid, as shown by Henninger :—

$$CH_2(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH_2\cdot OH \rightarrow CH_2{=}CH\cdot CH{=}CH_2,$$

and, by analogy, it is possible to conceive of a similar passage in the plant from dambose to derivatives of butadiene, such derivatives being, no doubt, subject to isomeric changes by intramolecular rearrangement. These various considerations render Hoffmann's hypothesis a very rational one.

Harries has had the same idea of viewing rubber as being derived from the sugars.

On referring to the constitutional formula which he has assigned to the fundamental molecule, it will be understood that by the condensation of a grouping derived from pentane—C_5H_8 or $CH_3\cdot C\cdot CH_2\cdot CH_2\cdot CH$—the rubber molecule is obtained in the same way as one obtains those of starch and grape sugar.

In the latter case the simplification of the molecule is brought about by hydrolysis ; in the case of rubber there would be an additional process, the reduction of the 5-carbon atom sugars. The pentose would be reduced to C_5H_8, which, condensing while in the nascent state, would yield $(C_{10}H_{16})_x$.

This suggestion derives further justification from the fact, referred to later, that when rubber is oxidised—by means either of oxygen or ozone—levulinic aldehyde is formed. The relationship of this aldehyde to the sugars has long been established ; carbohydrates, such as starch, when heated with acids, such as hydrochloric acid, yield levulinic aldehyde, and this aldehyde contains, moreover, the radicle C_5H_8.

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[1] *Étude sur les fécules*, Nancy, 1878.

If, therefore, rubber, like the sugars, yields levulinic aldehyde under certain conditions, there must be some close relationship between the two substances, and it should be possible to derive the one from the other.

Harries goes still further, when he supposes that all the terpenes are, in the same way, related to the sugars, and that they are formed as a result of the reduction of the sugars. The equation would run—

$$3(C_6H_{12}O_6) = C_{10}H_{16} + 8H \cdot COOH + 2H_2O,$$

and the process would, moreover, seem to explain the disappearance of the sugars and the formation of formic acid in plants which produce terpenes.

According to Harries, rubber would only be an intermediate product, which on depolymerisation would give rise to terpenes. How are these various transformations—which we should often find very troublesome to carry out *in vitro*—brought about in the plant? The changes evidently take place in the leaf; it is there, in fact, that the various bodies capable of acting upon the substances undergoing change are concentrated—such as the diastase, the co-ferments, and the catalysts which come into action under the influence of light.

We have already explained the catalytic rôle of chlorophyll. In these new reactions its own internal energy is clearly brought into play, but, on the other hand—and this constitutes the catalytic character of its activity—it assists in the rapid degradation of the photolytic energy of light. It probably also modifies the frequency of vibration, and thus helps to bring about, by means of sympathetic vibration, according to the ideas expounded by Daniel Berthelot, the rupture of the chemical bonds which maintain the stability of the various compounds concerned in the reaction.

Its action is completed by that of the diastase and co-ferments.

If, for a moment, Béchamp's theory of the formation of zymases be admitted, every living organism must, at any given moment, provide the ferments it requires to carry out the chemical transformations and modifications necessary to its existence, by modification of its protoplasmic granules; it is thus that barley produces the diastase with which everyone is familiar. This theory, which has lately been strongly opposed, gives a fairly plausible explanation of what must go on in rubber plants; it affords an explanation of the conversion of cellulose or starch into dambose, and of dambose into erythritol, under the influence of the specific diastases elaborated by the plant itself, the presence of which in all latices has been pointed out by Bouchut.

The action of the diastases is accompanied by that of the co-ferments. The latter are defined by Bertrand as compounds of a mineral and an organic substance which act, as transition compounds, either as oxidising or as reducing agents, according to the following scheme:—

$$H_2O_2 + P \rightarrow PO_2$$
$$PO_2 + A \rightarrow P + AO_2.$$

They are typified by *laccase*.

The presence of these bodies has been determined by Spence, not only in the coagulated rubber, but also in the latex of *Funtumia elastica;* the part which they play in the formation of rubber must be an extremely important one. It is from the fact of their presence, moreover, that Spence has drawn the conclusion that latex constitutes a reserve food for the plant; a conclusion which Vernet has found by experiment to be accurate in the case of *Hevea.*

If a rubber plant be kept in the dark—that is to say, under conditions in which the activity of the chlorophyll cannot be displayed—it will show on tapping a continuous fall in its rubber content, until the latter vanishes altogether. The latex is then destroyed, either to contribute to the formation of new tissues, or to provide, by its combustion, a portion of the energy of which the plant has been deprived through the absence of light.

By means of these different concomitant processes—photolysis, catalysis, diastatic and co-ferment action—an explanation is afforded of the way in which starch, cellulose, and sugars can be modified to give rise, if not actually to rubber, properly so called, yet at all events to the liquid terpenic substance which was identified by Weber in *Castilloa latex*, and which coagulates to elastic rubber on contact with the air or with acids.

It is probable that the albuminoid membrane which Weber referred to as enveloping the globule, is nothing but the whole collection of protein, diastases, and co-ferments which have reacted with the cellulose materials. Trécul has, moreover, demonstrated the existence of such an albuminous membrane in the starch grain.

Is Rubber derived from Terpenes?—Can rubber, contrary to the opinion of Harries, be derived from terpenes?

Given the close relationship between the substances indicated by the identity of their empirical formulæ, C_5H_8, the above hypothesis would seem at the first glance to be as tenable as that which supposes rubber to be derived from cellulose, starch, or sugar.

In the plant, if the work of Bruhn[1] be referred to, pinene—($C_{10}H_{16}$)—is formed direct, without any intermediate products, and from pinene solid resins, dipinene, or colophene, $C_{20}H_{12}$, are formed by condensation.

In order to produce rubber, the structure of which is absolutely different from that of pinene, it would, therefore, be necessary for the initial pinene to undergo decomposition, in the plant, into two molecules of *isoprene*, the intramolecular linkages being transposed.

If rubber is formed in this way, it is remarkable that, in the small number of investigations which have been carried out on the producing plants, isoprene has never been found, neither have terpenes been discovered except in very small quantity.

Alexander, for example, in his researches on *Guayule*,[2] found that this plant contains from 20 to 25 per cent. of substances extractable by acetone; 54 per cent. of this extract is soluble in petroleum ether, 31 per cent. in ordinary ether, and 15 per cent. in alcohol. On saponification, an acid allied to cinnamic acid, phenylacetic acid, and a sesquiterpene alcohol with an odour of camphor are found in the product. Finally, on treatment with steam, about 0·5 per cent. of an ethereal oil containing pinene, and an unidentified sesquiterpene, are obtained.

Rathje finds in *Hancornia* only hydrocarbons of high boiling point, varying from 190° to 205° C. Pinene is hardly ever found in latex, a natural result of the fact that pinene is not a colloid, and can be crystallised at a suitable temperature. Hence by osmotic action it should be able to pass quite readily through the walls of the vessels, which are impermeable to the colloid rubber.

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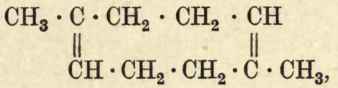
[1] *Chem. Zeit.*, 1900, 24, 105.

[2] *Ber.*, 1911, 44, 2320.

If rubber were derived from the terpenes, it is probable that the resins by which it is almost always accompanied in the latex, and which are precipitated with it on coagulation, would be completely saponifiable, since they would be oxidation products of pinene. But analysis has shown that the rubber resins are only saponifiable to a slight extent if at all, and that in most cases they are composed of secondary alcohols allied to cholesterol, and optically active.

For these reasons, however attractive the hypothesis of the formation of rubber from pinene[1] may appear, we are of opinion that it is less likely to be correct than that which regards rubber as derived from cellulose or starchy materials. But neither theory may be looked upon as demonstrated, and the true theory of the formation of rubber in the plant remains to be established.

On considering Harries' formula—



$$\begin{array}{llllll} CH_3\cdot & C & \cdot CH_2\cdot CH_2\cdot & CH & & \\ & \| & & \| & & \\ & CH & \cdot CH_2\cdot CH_2\cdot & C & \cdot CH_3, & \end{array}$$

it will be seen that compounds containing the following groupings may take part in the elaboration of the rubber molecule—

$$C\,\vdots\,,\ CH\,\vdots\,,\ CH_2\,:\,,\ CH_3\,\cdot$$

Theoretically, therefore, it is not impossible for sugars, starches, fats and oils, cellulose, resins, organic acids, and formaldehyde to be regarded as amongst the raw materials for the production of rubber.

If, as we believe, the seat of these changes is in the leaf, the permanent separation of those parts containing chlorophyll from those in which the latex circulates would lead to the idea that the formation of rubber is due to secondary changes.

Further proof would seem to be afforded by Vernet's observation that the rubber content of the *Hevea* seed embryo increases on germination.

Function of the Latex.—The determination of the exact rôle of the latex in the plant economy is of the greatest interest, because of its bearing upon the methods of exploiting rubber plants. If, for instance, the latex is a waste product, there should be no danger to the tree in draining it completely.

If, on the other hand, it plays a part in plant nourishment, tapping must be carried out on a very carefully thought-out system.

There is by no means agreement of views on this point; discussion on the functions of the latex is still going on, although it is admitted that the sole object of the tree in producing latex is not to supply mankind with rubber.

Our view is that the latex may be either a source of nutrition to the plant or a waste product, according to the species which produces it.

Plant latex had attracted the attention of botanists as far back as the end of the seventeenth century, and even at that time the difficulty was recognised of classifying it in one of the two groups of products which were regarded as resulting from the life activity of all plants—viz., alimentary materials, useful to the plant, and waste or excretionary products, which are useless to it as food.

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[1] Wildemann, *Caoutchouc et Guttapercha,* 1909, 6, 3190.

As a matter of fact, latex contains, in greater or less quantity, according to the plant, substances useful to its development, but at the same time there are present obvious waste products of the chemical reactions going on within the living cell. According to the preponderance of one or other of these two groups, according also to the individual bias of the observer, botanists had come to regard the laticiferous system sometimes as a reservoir of plant foods, sometimes as a sump in which were accumulated substances which might interfere with the proper circulation of products useful to the life of the plant. Latterly we have obtained more definite knowledge as to the rôle of the latex.

The researches of Sachs have shown that its composition varies with the conditions of lighting—a perfectly normal state of affairs in view of the principles of plant assimilation which have already been set forth.

Such an observation favours the utilisation of the materials to the profit of the plant.

Haberlandt has gone a step further, and has shown that the starch grains which we have pointed out are present, notably in the latex of *Euphorbia*, disappear when the plants are left in the dark for two or three weeks.

It is, therefore, probable that certain constituents of the latex which are nutritive in character can be again made use of by the plant.

The presence of cell nuclei in certain latex tubes, and the position of the latter in the leaves, afford further evidence that the latex serves as a food. It is also likely that it receives the products of assimilation by the leaf chlorophyll, and thus carries, to other parts of the plant, the carbohydrates then present in their transport form.

The other view has had its supporters.

In the case of *Hevea*, which may be taken as typical of rubber-yielding trees, we shall see that the latex consists of water containing, in suspension, globules of rubber and of resins, and, in solution, sugars, proteins, and mineral substances.

But several of these substances can obviously not be regarded as constituting reserve nutriment. In fact, no one has ever been able to demonstrate the utilisation of ready-formed rubber in the plant, and it is upon this fact that the definition of latex as an excretionary product was originally based.

Observations made by Wright[1] have shown that the suppression of the laticiferous vessels does not injuriously affect the life of the tree, and the conclusion has been drawn that the latex which they contain does not serve to nourish the plant.

At one time the ideas of Warning were even looked upon with favour; according to him the latex has no other function than that of constituting a reserve supply of water for the dry season; this theory received the support of Parkin and Ridley.

Others, with de Vries, regarded the latex as destined, more particularly, to play a part in the healing of wounds received by the tree, and from that idea Kneipp made the deduction that its rôle is essentially protective.

A comparison of these various observations, combined with an examination of the very different conditions of life of the various rubber plants, will lead to the conclusion that it is almost impossible to assign a single function to latex.

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[1] *Hevea Braziliensis*, London, 1906, p. 7.

Its function seems to be multiple in character. It appears to be equally probable that it must serve as a reservoir of nutritive substances, that it must form a vehicle for the transportation to various parts of the plant of the materials necessary for its development, and that it constitutes a reserve supply of water. It is equally without doubt that the contents of the laticiferous vessels do serve to defend the tree against the attacks of certain insects. Finally, it appears that, in addition, by spontaneously coagulating when exposed to the air, it facilitates the cicatrisation of wounds, by covering them over and thus shielding the plant tissues from the oxidising action of the air, and from the attack of micro-organisms.

Vernet, in his work on *Hevea*, has carried the investigation to great lengths with a view to finding out what actually is the rôle of latex in the plant.[1] This study, which is quite recent, seems to solve the problem, and we shall reproduce it *in extenso*.

" In the case of *Hevea*," he says, " ought we to regard the latex and the rubber as excretionary or as alimentary products ?

" On the way in which this question is to be answered depends the whole system to be adopted in tapping, and consequently the rational exploitation of rubber trees; the great importance of the problem will, therefore, be appreciated.

" In support of the view which regards latex as a waste product there are two facts, one of a general character, the other experimental. For a long period it has been considered that plant secretions are excretionary products when the plant diverts them into closed cavities, where they remain imprisoned during the whole life of the plant, and are thus withdrawn from all contact with the liquid food materials.

" But as latex vessels are far from being closed cavities—since, as we have already seen, they form a system of sieve tubes and are made up of cells freely anastomosed tangentially—this first piece of evidence can be contested.

" Further, the quantity of latex in the plant varies at different times, and according to Trécul's theory, it is impossible to regard as excretionary a product subject to such variations in quantity."

The experimental proof of the excretionary character of latex rests upon the observations of Warning and Parkin, whom we have already quoted, and their experiments consisted in partially removing the bark from a *Hevea* without killing it. This experiment was repeated by Vernet, who completely severed the latex vessels of a *Hevea* tree, and found that it entirely lost its leaves, and that it suffered from the treatment. From this experiment, therefore, it does not appear that the latex is an excretionary product, the presence or absence of which is immaterial to the plant, and, in fact, this thesis is only upheld to-day by a few botanists; the greater number are of the opposite opinion.

Trécul and Faivre think that the latex is a reserve material; Baillon regards it as supplying the place of the liberian sap; Schullerus says that " the laticiferous system takes from the various tissues the materials necessary for building up the meristem, and carries them rapidly to it"; and, lastly, Treub writes " the latex tubes of the *Euphorbias* assist in the translocation of starchy substances, the starch being in a transport form."

Vernet, still more categorically, says that the latex, as a whole, is a food indispensable to the life of the tree, and he supports his opinion with three

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[1] *Caoutchouc et Guttapercha*, 1910, 7, 3808.

kinds of evidence: evidence from analogy, evidence of chemical composition, and evidence drawn from the effects of tapping.

The laticiferous vessels, as has been seen, are, morphologically, strikingly similar to the sieve tubes—that is to say, to the recognised organs of circulation and nutrition in the plants in which they occur. The abundance of the latex vessels, which are the more numerous the nearer they are to the generative layer, would lead to the assignment of a nutritive function to the substances which they contain.

In all organs in course of formation, or in course of growth, latex is found; it is present even in the embryo of the seeds, and is found in the young plant whilst it is being nourished solely by the *cotyledons*.

This one fact, apart from all others, would be sufficient to show that latex is not an excretion. The very composition of latex is suggestive, for it contains not only water and rubber, but also, as we shall see from its analysis, materials which everyone knows are indispensable to the nutrition of plants, such as sugars and starch.

Lastly, on tapping a *Hevea* tree and following the increase in the girth of the trunk during the period of tapping, it is found that the rate of increase becomes less than the normal, and that when tapping ceases the reverse takes place.

These facts can only be explained, the first by a diminution in the intensity of nutrition; the second by a greater cellular activity, which begins as soon as the object of experiment is able to make use, for its own purposes, of the substance of which it had been deprived. The diminution in weight of the seeds when the trees are being tapped is yet another argument in favour of the nutritive value of latex.

These various facts show, almost conclusively, that at all events in the case of *Hevea*, and probably also in the case of all rubber plants, the latex plays an important part in plant nutrition.

It seems, therefore, to follow from Vernet's work, as well as from Wildemann's observations, that the latex cannot be regarded as a waste product which may be removed from the tree with impunity. It further follows that the methods employed in winning the commercial product from the trees containing it must be such as not to injure the tree.

These considerations are in agreement with another observation of Vernet, with regard to *Hevea* and *Ficus*.

"If," says Vernet,[1] "an incision ½ to 1 cm. in depth be made in the trunk, branches, or roots of a *Hevea* tree, or if one of its leaves, one of its flowers, or one of its fruits be cut off, the white liquid from which rubber is produced will be seen at once to make its appearance."

Such an operation must not be carried out carelessly, but in such a way as to protect from injury the liberian tissue, in which the latex tubes are situated, and at the same time to obtain from the tree all the rubber which it is capable, economically, of yielding.

Hence arises the multiplicity of suggested methods of tapping with the hatchet, V-tapping, herring-bone tapping, spiral tapping, pricking, etc., etc.[2] From observations made under practical conditions, it has been shown that the quantity of rubber obtained by means of smallish wounds increases with

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[1] Studies on Tapping, *Caoutchouc et Guttapercha*, 1909, 6, 3312.

[2] Clarkson has constructed an apparatus for removing latex from the tree by suction with a minimum number of wounds. Such an apparatus can obviously only be of use in the case of anastomosed systems of latex vessels.

their number up to a certain limit, beyond which the amount obtained is no longer proportional to the number of the daily incisions.

The elaboration of rubber and of latex is, in fact, a continuous function of the plant's life activity; it is impossible to make the plant produce more rubber than its organs are capable of elaborating, or more latex than the daily excess of its laticiferous vessels.

The flow of latex is not continuous; after tapping operations have been carried out it slows down, when the pressure within the vessels has appreciably diminished as a result of the exudation. This slackening allows the rubber to coagulate, more or less rapidly, on the wounds, and so to put a stop to the process of bleeding.

The yield per tapping is, therefore, proportional to the pressure within the latex tubes and inversely proportional to the speed of coagulation.

The effect of climatic and physiological influences on the yield are very marked, and must be observed in order to arrive at the conditions for maximum yield. Thus it is known that, when the leaves fall, the exudation is considerably diminished.[1] If these factors be neglected, and tapping be carried out in an intensive fashion, the proportion of rubber in the latex falls off rapidly. Mathieu states that "certain trees in Ceylon which at first gave one pound of rubber per three pounds of latex, degenerated in this respect, under the influence of intensive and haphazard tapping, to the point of yielding a latex containing 10 per cent. of rubber and 90 per cent. of water."[2]

Another question, *à propos* of the latex, suggests itself—that is, as to whether the rubber as collected is of old or recent formation.

Knowing that a rubber tree cannot be tapped before it has reached a certain age, it has been thought by some that the plant elaborated the rubber and kept it in reserve. This is hardly likely, because the rubber has its origin in newly formed tissues.

Wildemann says that it is rather to be assumed that the age of the tree comes in, in enabling it to stand the series of internal physico-chemical reactions involved in the formation of rubber, and which a very young plant is not fitted to undergo. The difference which exists between the latex of young trees and that of old ones, and the difference in their rubber content, show that this hypothesis is well-founded.

Difficulties are met with in attempting to extend to other latices than that of *Hevea*, the theory which views the latex as reserve nutriment; in *Ficus*, for example, which differs entirely from *Hevea* from the histological point of view, and in which the latex vessels do not anastomose but form closed cavities, the latex does not appear to be a reserve food.

It seems rather to be a simple waste product which would go on accumulating in the interior of the latex vessels. This explains why, when old, unworked trees are tapped for the first time, there is such an abundance of latex.

In What Form is Rubber present in the Latex ?—The study of latex from the analytical point of view is also not in a very advanced state, and dis-

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[1] February and March are bad months for production. According to Tromp de Haas, the proportion of solids contained in the latex falls off 30 per cent. between the first and the last tapping, whereas the nitrogen content and the percentage of mineral matter increases.

[2] *Culture de Caoutchouc Para.*

cussion is still open on the question as to whether the rubber is present in it as such, or whether it exists there in the form of a liquid polyterpene.

It is practically only in the researches carried out by Weber on *Castilloa*, at the time of his journey to Mexico, in the papers by Jumelle, Ditmar, and Victor Henri, or in the studies of Vernet during his visit to Indo-Oceania, that interesting information on this subject is to be found.

Moreover, on many points we shall find ourselves met by great differences of opinion. Whereas Harries holds the view that rubber exists ready formed in the latex,[1] Weber says [2] that it exhibits such peculiar properties that its existence, in the form of actual rubber, has always appeared to him paradoxical.

Investigation on this subject is, moreover, very difficult, owing to the rapidity with which, even in presence of ammonia, the latex becomes modified and spoilt, or coagulates. For this reason no confidence can be placed in analytical results obtained in Europe with samples which have certainly been spoilt during their passage here. Moreover, is there not already some difference between the latex as collected on tapping, and the latex as it circulates in the tree?

We do not know very much on this subject, nevertheless it is almost certain that in the case of *Hevea*, for example, the state of the latex in the laticiferous vessels is not the same as at the moment of liberation from the tree as the result of tapping.

The following experiment of Vernet's supports this view:—It is known that if freshly collected latex be heated, it is rapidly coagulated, and a clot of rubber is obtained. If a branch of a living *Hevea* be heated in the same way, and if the bark and the liber be afterwards broken across, one is surprised to find, in the laticiferous vessels, not, as one would have expected, elastic filaments of coagulated rubber, but only a plethora of sap.

This observation seems to demonstrate, contrary to the opinion of most planters, who believe that rubber exists ready-formed in the tree, that the latex which circulates in the *Hevea* tree, does not behave in the same way, under the influence of heat, as the latex extracted by tapping.

Hence it may be concluded that they are not in the same state, but that there has been some modification of structure in the one case, or that a condensation has taken place under the influence of light, heat, or air.

The results obtained on trying to extract rubber direct from rubber trees by means of solvents, in most cases confirm Vernet's observation, although Prager has succeeded in extracting a good quality rubber in excessively small quantity from *Hevea* leaves.[3]

Perrier de la Bathie, in the case of the Madagascar *Lombiro*, and Schlechter, in the case of *Manihot*, obtained by direct extraction only a tacky rubber containing a low percentage of true caoutchouc. Working with the branches or the leaves of young *Heveas*, two or three years old, Parkin appears to have collected an intermediate substance, to which he has given the name *Viscine*.

Weber, in the course of an investigation on *Castilloa*, the details of which will be gone into later, separated rubber in the form of a viscous oil, which

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[1] Lecture at Vienna, March 12, 1910.

[2] *Ber.*, 1903, 36, 3108.

[3] Generally speaking, the leaves and the small branches of most rubber trees do not contain rubber. In herbaceous plants, rubber is found in the roots and rhizomes, and not in the stem.

could be coagulated either by evaporation or by the addition of acids. In the case of these various plants, then, it would appear to be permissible to regard the substance found in the collecting cups as not being identical with that which circulates in the laticiferous vessels.

It would not do, however, to apply these conclusions too generally, for although from the same plant it may be possible to obtain two distinct products, the one elastic and the other syrupy, and although it may be impossible, in the case of plants like *Hevea,* to find coagulated rubber in the latex vessels, yet, on the other hand, long elastic filaments are invariably found when a dried fragment of a *Landolphia* or of an *Ecclysanthera* is broken across.

From certain Madagascar lianas Gerber was able to obtain from 5 to 8 per cent. of ready-formed rubber.[1] The composition and properties of *Ficus* latex vary according to whether it is derived from the upper or the lower parts of the tree; that obtained from the leaves and the green bark often cannot be coagulated; that derived from the adult trunk, on the contrary, gives an elastic rubber, of good nerve. In view of such contradictory results, one is tempted to support the conclusions drawn by Bertrand from the results of his investigations on tackiness, of which we shall speak later:—" I have been forced to admit the existence of several, distinctly different types of rubber, the difference not being a result of the methods of collection or of coagulation employed, but depending only upon the botanical origin—that is to say, upon the species of plants from which the rubbers are obtained."

One might say: " So many rubber plants, so many latices."

This idea would be, moreover, in perfect agreement with the very definition of the process of secretion given by Baillon:—" Secretion is the manifestation of cell life, and its products should, both in plants and animals, play distinct and often mutually antagonistic parts."

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[1] The rhizomes of *Actinella* contain 10 per cent. of coagulated rubber.

CHAPTER VI.

PHYSICAL AND CHEMICAL EXAMINATION OF LATEX.

Physical Examination.—Under ordinary conditions latex, as obtained by tapping—for example that of *Hevea*—presents the appearance of a white liquid, having about the same consistency as cow's milk, more or less thick according to the amount of rubber it contains, which depends upon the height above the ground at which the latex was taken from the tree, and upon the age of the latter. This latex stains the hands black, and when left exposed to the air develops an odour of methylamine.

Its density varies according to the amount of rubber it contains, and, according to Linder and Marckwald and Frank, the richest latex is that with the lowest specific gravity.

Ure has determined the density of several latices and has found it to be 1·0175 in the case of a sample having the consistency of a thick cream, and containing 37 per cent. of rubber; and 1·04125 in the case of a more fluid sample, containing only 20 per cent. of rubber. Muspratt estimates the average density as not exceeding 1·012, but, on the other hand, Victor Henri has found latices having a density of only 0·973, yet containing only 8·7 per cent. of rubber.

Lindet has published some results obtained by Aimé Girard giving the rubber content and the density of a number of latices; coagulation was effected by means of alcohol:—

GIRARD'S TABLE.

Botanical Origin.	Density.	Rubber Content.
		Per cent.
Hancornia, ...	0·990	31·6
African lianas, . . .	0·987	33·4
Siphonia (Para), . . .	0·986	42·6
Castilloa, ...	0·980	32·3
Ficus macrophylla, . .	1·000	37·5
,, elastica, . . .	1·001	17·3
,, nitida, . . .	0·971	31·3
,, levigata, . . .	1·005	28·0
,, kickxia, . . .	1·005	27·0

Vernet has succeeded in drawing up a table showing the content of *Hevea* latices in rubber precipitable by 90 per cent. alcohol,[1] employing for his density determinations an exceedingly ingenious pyknometer-dilatometer of his own invention. It consists of a glass vessel of 50 c.c. capacity, provided with two openings, one of which is fitted with a stopper carrying a ther-

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[1] *Caoutchouc et Guttapercha,* 1910, 7, 4553.

mometer, graduated in half-degrees Centigrade, whilst the other is elongated into the form of a tube graduated in tenths of a c.c., starting from the 50 c.c. level of the apparatus. The length or the capacity of this tube must be such that when the thermometer stopper is fitted into the filled apparatus the liquid will not rise in the tube above the limit of the graduations. By means of this device readings of volumes can be taken direct.

In order to plot the curves necessary for the construction of a table of rubber contents, the necessary figures must be obtained experimentally by the following series of operations :—

1. The pykno-dilatometer is weighed empty.
2. The vessel is filled with the latex from a pipette, care being taken to avoid introducing air-bubbles. To this end the vessel is inclined and the latex allowed to flow from the pipette down the side-walls; as the latex fills the vessel it is gradually restored to a vertical position. Any bubbles which may have been formed on the surface can be removed by sucking them up into a pipette.
3. The thermometer-stopper is inserted gently into the opening, the excess of latex being allowed to overflow; care must be taken to avoid air-bubbles between the stopper and the latex.
4. The latex is allowed, if necessary, to attain the temperature of the surrounding air, and its volume is then noted, together with the temperature, the usual corrections being made.
5. The apparatus is cleaned by pouring a little alcohol over the latex which has overflowed in order to coagulate it, and then removing it by means of filter paper, afterwards wiping it over with a piece of fine cloth.
6. The vessel containing the latex is weighed, and the net weight of the latex is obtained by subtracting the tare of the vessel.
7. The density of the latex at the prevailing temperature is calculated from its ascertained weight and volume.
8. The variation of density with temperature is determined by taking readings of volume at different temperatures, to which the apparatus is brought by immersing it in water at such temperatures contained in a calorimeter.
9. Curves are drawn, plotting temperatures as abscissæ and densities as ordinates.
10. A volume of 90 per cent. alcohol equal to that of the latex in the pyknometer is measured out in a graduated test-tube; the latex is then poured into a small crystallising dish, and the pyknometer rinsed out with the alcohol, the pellicles of rubber formed being added, with the alcohol, to the latex in the dish, the contents of which are then stirred. Finally, the dish is covered to prevent evaporation.
11. The coagulated rubber is washed several times with 90 per cent. alcohol, and is then pressed into the form of a thin biscuit, dried *in vacuo* over sulphuric acid, and weighed.
12. From this weight and the volume of the latex at different temperatures a simple calculation enables us to obtain the amount of rubber in unit volume or weight of latex at different temperatures, or in latices of different densities at the same temperature.

The temperature selected by Vernet for his table was 20° C.

13. A curve showing the rubber content at 20° C. is drawn, plotting densities as abscissæ and percentages of rubber as ordinates.
14. A curve drawn with temperatures as abscissæ and percentages of

rubber as ordinates will show the amount of rubber in a given latex at different temperatures.

15. The correction for washing is found by determining the loss in weight on washing the alcohol coagulum.

With Vernet's table it is, therefore, possible to ascertain at once, by simply reading a densimeter and a thermometer, the amount of rubber coagulable by alcohol, and by applying the ascertained correction, even of washed rubber, present in a given sample of *Hevea* latex.

In order to apply the table to other latices the necessary correction must be determined by actual coagulation trials.

Thus with *Landolphia Heudelotii* latex the experimental figure is 40·7 per cent. of rubber, whereas the table gives 39·1 per cent. The difference, 1·6 per cent., is, therefore, the correction to be added to the figure obtained from Vernet's table. When a laboratory is available it will always be better to draw up a table, on the lines explained, for the particular latices to be dealt with.

All determinations must be made with the fresh latex, without addition of water.

A portion of Vernet's table,[1] from a density of 0·960 to 0·991, and between temperatures of 18° C. and 30° C., is here reproduced :—

VERNET'S TABLE.

Densities.	18°	19°	20°	21°	22°	23°	24°	25°	26°	27°	28°	29°	30°
0·960	51·4	51·3	51·0	50·9	50·7	50·4	50·2	49·9	49·6	49·3	49·0	48·7	48·3
0·961	51·0	50·8	50·6	50·4	50·2	50·0	49·7	49·5	49·2	48·9	48·6	48·2	47·6
0·962	50·6	50·5	50·3	50·1	49·9	49·7	49·4	49·1	48·9	48·5	48·2	47·9	47·5
0·963	50·2	50·1	49·9	49·7	49·5	49·3	49·1	48·8	48·5	48·2	47·9	47·6	47·2
0·964	49·8	49·7	49·5	49·3	49·1	48·9	48·7	48·4	48·1	47·8	47·5	47·2	46·8
0·965	49·4	49.3	49·1	48·9	48·7	48·5	48·3	48·0	47·7	47·4	47·1	46·8	46·5
0·966	49·0	48·9	48·7	48·5	48·3	48·1	47·9	47·6	47·3	47·1	46·8	46·4	46·1
0·967	48·6	48·5	48·3	48·1	47·9	47·7	47·5	47·2	47·0	46·7	46·4	46·0	45·7
0·968	48·1	48·0	47·8	47·6	47·4	47·2	47·0	46·8	46·5	46·2	45·9	45·6	45·2
9·969	47·6	47·5	47·3	47·1	46·9	46·7	46·5	46·3	46·0	45·7	45·4	45·1	44·8
0·970	47·1	47·0	46·8	46·6	46·4	46·2	46·0	45·8	45·5	45·2	45·0	44·7	44·3
0·971	46·6	46·5	46·3	46·1	45·9	45·7	45·5	45·3	45·0	44·7	44·4	44·2	43·8
0·972	46·1	45·9	45·8	45·6	45·4	45·2	45·0	44·8	44·5	44·2	43·9	43·6	43·3
0·973	45·5	45·4	45·2	45·0	44·8	44·7	44·5	44·2	43·9	43·7	43·4	43·1	42·8
0·974	45·0	44·8	44·7	44·5	44·3	44·1	43·9	43·7	43·4	43·1	42·9	42·6	42·2
0·975	44·3	44·2	44·0	43·9	43·7	43·5	43·3	43·0	42·8	42·6	42·3	42·0	41·7
0·977	43·7	43·6	43·4	43·2	43·0	42·9	42·7	42·5	42·5	41·9	41·7	41·4	41·1
0·978	43·0	42·9	42·8	42·6	42·4	42·2	42·0	41·8	41·6	41·3	41·0	40·7	40·04
0·979	41·6	41·5	41·3	41·1	41·0	40·8	40·6	40·4	40·2	39·9	39·7	39·3	39·1
0·980	40·8	40·7	40·6	40·4	40·2	40·0	39·9	39·7	39·4	39·2	38·9	38·7	38·4
0·981	40·0	39·9	39·8	39·6	39·4	39·3	39·0	38·9	38·6	38·4	38·2	37·9	37·6
0·982	39·2	39·0	39·0	38·8	38·8	38·5	38·3	38·0	37·9	37·6	37·4	37·1	36·9
0·983	38·3	38·2	38·0	37·9	37·8	37·6	37·4	37·2	37·0	36·8	36·5	36·3	36·0
0·984	37·4	37·2	37·1	37·0	36·8	36·7	36·5	36·3	36·1	35·8	35·6	35·4	35·1
0·985	36·3	36·2	36·1	35·9	35·8	35·6	35·4	35·3	35·0	34·8	34·6	34·4	34·1
0‘986	35·2	35·1	35·0	34·8	34·7	34·5	34·4	34·2	34·0	33·8	33·6	33·3	33·1
0·987	34·0	33·9	33·8	33·7	33·5	33·4	33·3	33·1	32 9	32·7	32·5	32·2	32·0
0·988	32·8	32·7	32·6	32·5	32·3	32·2	32·1	31·9	31·7	31·5	31·3	31·1	30·8
0·989	31·6	31·5	31·4	31·2	31·1	31·0	30·8	30·7	30·5	30·3	30·1	29·9	29·7
0·990	30·2	30·1	30·0	29·8	29·7	29·6	29·4	29·3	29·1	28·9	28·8	28·5	28·3
0·991	28·6	28·6	28·5	28·5	28·2	28·1	28·0	27·8	27·7	27·5	27·3	27·1	26·9

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[1] See Vernet's table, *Caoutchouc et Guttapercha*, 1910, 7, 3896.

The corrections for washed, dried rubber are as follows :—

Natural coagulation,	0·829
Smoke ,,	0·885
Acetic acid ,,	0·973
,, ,, and formaldehyde coagulation,	0·988

Microscopic examination of the latex as it leaves the tree reveals the presence in it of globules, from 0·8 to 1·5 micromillimetres in diameter; they are arranged in rows, somewhat after the manner of streptococci, and, according to Weber, are surrounded by a very thin albuminous membrane.

Victor Henri, in his investigation of latices,[1] has examined this particular form of rubber with great care. "*Hevea* latex," he says, "is composed of ovoid, nearly spherical, globules, having an average diameter of one thousandth of a millimetre."[2] Under high magnification these globules are distinctly seen to be in continuous Brownian movement.

Using a magnification of 600 diameters, Victor Henri has made a series of cinematographic reproductions of latex, at the rate of 20 exposures per second, and these have enabled him to study on the one hand the Brownian movement in the pure latex, and, on the other, the movement of the globules after the addition of varying quantities of acids, alcohols, alkalies, and salts.

The Brownian movement is exceedingly irregular, and the free paths of the globules are considerable; if a little soda be added there is no apparent change in the mass and no coagulation, but the amplitude of the globular vibration is diminished; with traces of acetic acid, although no coagulum is formed, the Brownian movement is almost completely held up.

The mean of the displacements occurring in $\frac{1}{20}$ of a second is found, by actual measurement, to be :—

$\mu\mu$ 62 in the pure latex.
$\mu\mu$ 31 ,, latex after addition of alkali.
$\mu\mu$ 07 ,, ,, ,, ,, acetic acid.

It is very difficult to give an explanation of these changes; one may suppose that around each globule a zone of adhesion is formed, in which either acid or alkali is present in higher concentration than in the intervening liquid.

Victor Henri's experiments, described later, seem to justify this hypothesis.

It was further of interest to ascertain the number of globules contained in a given volume of latex, because such a figure might give a very exact indication of its value. In order to make this determination it was necessary to arrest the Brownian movement, without bringing about coagulation. This can be done either by diluting the latex with water, or by adding a 20 per cent. solution of pure sodium chloride. When the globules were counted under the latter conditions the average figure obtained by Victor Henri was 50 million globules per cubic millimetre.

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[1] Communication to the International Congress in London, 1908.

[2] According to Maréchal and Laurent the diameter of the globules varies with the height at which the latex is tapped, and the larger globules coagulate the more readily. They also vary according to the plant, those of *Funtumia* being about 2½ times as large as those of *Hevea*.

In the light of these observations, latex appears to be an emulsion of rubber in water holding in solution (or suspension) glucosides, sugars, resins, albuminoids, enzymes, organic acids, and mineral salts.

It is the presence of the glucosides and the sugars which confers on the latex its characteristic flavour, which has been compared by Carrey to that of cow's milk.

Variability of Composition.—Its composition is not constant, but varies within very wide limits, according to the plant producing it, and the method, season, and height above ground level, of the tapping.

Thus from a *Ficus* plant, 7 feet 4½ inches high, Adriani obtained—

At a height of	12 inches	a latex	containing	25·15	per cent.	of rubber.
„ „	5 ft. 6 in.	„	„	24·05	„	„
„ „	6 ft. 10½ in.	„	„	20·90	„	„
At the top		„	„	17·70	„	„

The age of the tree also has an influence upon the richness of the latex. Weber found the percentage of rubber in the latex of a *Castilloa* tree to be—

At 6 years old, ...	26 per cent.
„ 7 „ „	27 „
„ 8 „ „	29 „
„ 9 „ „	31 „

The same is to be observed in the case of *Hevea*, with which Vernet obtained average percentages varying from 40 to 42 per cent., and in general the same applies to all plants which can be exploited by tapping.

We are, therefore, in a position to-day to lay down the axiom that a rubber tree should not be exploited before it is ten years old.

In the case of the *lianas* the rubber content is often higher. Jumelle and Perrier de la Bathie have handled latex from Madagascar containing 44 and even 64 per cent. of rubber. The richness of the latex appears to increase during the hot weather. The climate, as well as the humidity of the atmosphere, seems to have a very important influence upon the rubber content, but, unfortunately, no systematic study of this subject has been made.

Having reviewed rapidly the physical properties of this very complex liquid, we will pass on to its chemical examination.

Chemical Examination.—Since it is composed essentially of two different portions, a colloid-rubber, and a serum, it possesses the characteristics of a colloidal solution, or *sol*, and its investigation becomes of a particularly delicate character.

The chemical study of latex is of no less importance than its physical examination, for on it must be based the methods of coagulation, on which the whole value of the rubber depends, as well as the purification processes, by the aid of which a rubber free from defects can be prepared.

First, on the qualitative side, when taken from the tree latices are alkaline to litmus; it appears that the sugars present in the serum undergo fermentation, yielding acetic and butyric acids; this fermentation is made use of in Africa, assisted by evaporation of the water, to bring about coagulation of the rubber. According to Adriani alkalinity of latex is a property peculiar to *Hevea*, and *Ficus* serum is acid when taken from the tree, the acidity being due to a particular organic acid, the alkali (potassium and sodium) salts of which are insoluble, whilst its calcium, magnesium, and iron salts are soluble in water.

Jumelle, in his work, *Plantes à Caoutchouc*,[1] divides latices into two classes, the alkaline and the acid, and regards this classification as of great importance in connection with the determination of the most suitable methods of coagulation.

In Brazil it is usually considered that a latex can be kept without alteration for twelve hours. In Tonkin, Java, and Ceylon it is found to be necessary to add water to it in order to prevent its decomposition within that period of time.

According to Weber, latex turns brown pretty quickly when left exposed to the air, and even becomes almost black in a few hours. These changes are due to the action of oxydases, the presence of which in the latex may be demonstrated by the blue colouration developed on iodide of starch paper. In contact with the air latex gives, after a considerable time, and without heating, a coagulum which, when examined microscopically, is found to possess a highly reticular structure; optical examination, according to Chapel and Tempère, reveals the presence in it of two substances, one compact, the other softer, which have been termed the hard and the soft matter. Lastly, if spontaneous change in the air be allowed to go on to completion, the latex assumes the appearance of a kind of tar, and the rubber which separates from it is very sticky; in colour it is iron-grey tinged with greenish-yellow, very unpleasing in appearance.

Spence showed in 1908 that latex contains enzymes, and Kaye that oxydases are present in it; these bodies play a large part in bringing about the changes we have just referred to.

Spence holds that the enzymes set the reactions going, but that in reality the oxidation processes are due to the oxidases. This point has been studied by Harries, and we shall have occasion to return to it when considering methods of analysing coagulated rubber. When water is added in small quantity to latex, no change in the grouping of the globules is brought about, but great dilution causes them to separate and form a creamy layer.

According to Weber,[2] if, after dilution with water, the latex be shaken up, a homogeneous emulsion is not again obtained, small clots about the size of a lentil remaining in suspension. These can, however, be split up and made to disappear by heating the diluted latex, leaving a homogeneous mixture, indistinguishable from ordinary latex.

This effect of heat on a diluted latex containing clots is very curious, for, as a rule, heat is a means employed to coagulate the rubber in a normal latex.

These points have been contested by Tromp de Haas and de Jong.

According to Adriani, when 90 per cent. alcohol is added in excess to rubber latex, nuclei are formed, which soon change into groups of crystalline needles (?) Ordinary ether has a similar effect.

Acids in general, either organic or mineral, arrest the Brownian movement in the latex, and determine the grouping together of the suspended globules; they act, therefore, as coagulants.

Concentrated sulphuric acid, and hydrochloric acid in aqueous solution, convert them into a compact substance, often viscous and of a brown colour.

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[1] Published by Chalamel, 1903.

[2] *Ber.*, 1903, 36, 3168.

This reaction, combined with the addition of phenol as an antiseptic, has been employed by Dr. Morisse, in place of smoking, for the rapid coagulation of rubber latex.

Concentrated acetic acid, formic acid, citric acid, and most of the stronger organic acids also bring about rapid coagulation. The globules join up with one another, increasing in volume two-fold, but maintaining their original shape. Their diameter increases from 0·8 to 1·05 micromillimetre, according to Adriani. Coagulation by means of acetic acid is generally employed for plantation rubber, trichloracetic and formic acids being also used. Citric acid is favoured in equatorial Africa and in Madagascar. Hydrochloric acid is a powerful coagulant; a current of the gas passed into the latex produces immediate coalescence of the globules; and, on the other hand, if a viscous rubber be subjected to its action it soon loses its stickiness, regains its elasticity, and is converted into a rubber of good quality. If the treatment be prolonged a very appreciable rise in temperature is observed, the rubber hardens, and tends to become transformed into a substance somewhat resembling ebonite. This is the result of chemical combination between the rubber and the acid, the product formed being analogous with that obtained with hydrobromic acid. We shall have occasion to return to these reactions when dealing with rubber in the coagulated state.

Carbon dioxide appears to be an excellent coagulant, and, very probably, plays a leading part in the method of smoke coagulation. Pahl, who has made a study of the smoke produced[1] by the combustion of the Urucuri palm nuts used in Amazonia, found no particularly active compound in it, and so he attributes to the carbon dioxide present the property of coagulating the rubber.

Applying an idea which had been suggested by Alexander in connection with the treatment of reclaimed rubber, Pahl atomises the latex and brings it into contact with carbon dioxide under pressure in a special apparatus. In its finely divided state, the globules of the latex are easily attacked by the gas. Concentrated nitric acid, which, we shall see presently, reacts energetically on coagulated rubber, does not attack rubber in its nascent state. On the other hand, in certain cases, as for example that of *Ficus* latex, it attacks the serum and produces a white, filmy precipitate. When this is isolated it can be redissolved and crystallised; it appears to be a compound of magnesia with various organic acids.

The presence of magnesia in the serum of rubber trees is interesting, for it is known that this substance plays an important part—probably as catalyst—in all reactions in which chlorophyll is involved.

Potash, soda, and ammonia appear to have no action on the globules; they only produce a yellow or greenish-yellow colouration in the serum, which becomes more transparent, and loses its opalescence. Seeligmann holds, and rightly, that although these bases do not modify the globules in a chemical sense, they have nevertheless some action upon the latex, since they prevent coalescence, and maintain a state of high dispersion within the serum. This is particularly the case with ammonia, and the property has often been put to account in order to preserve latex; in such cases the ammonia used is of 7 to 8 per cent. strength.

Rubber is precipitated when either sodium chloride, mercuric chloride, phenol, or ammonium fluoride is added to latex.

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[1] *Gummi Zeit.*, 1910, 24.

A similar result follows the addition of ferric chloride, but is accompanied by some curious phenomena. According to Weber, this salt produces a deep green colouration in the serum; this reaction, which is analogous to that of tannin, is not due to the presence of this substance in the latex, but rather to the presence of glucosides, which, in a centrifuged serum, give a greenish-black precipitate with ferric chloride.

Potash alum, recommended by Strauss, hydroferrocyanic acid, tannin, and in general all protein precipitants, behave towards latex as coagulants. It is the same with acetone; on the other hand, formaldehyde is, according to Ditmar, without action, even when heated.

Tincture of iodine stains the globules brown, and causes them to unite to form a viscous mass which can be drawn out into long elastic threads; Morisse's view is that this reaction is due entirely to the alcohol in the tincture.

Complete analyses of latex from various sources have been made at different times, and some of them are reproduced below:—

HEVEA BRAZILIENSIS (*Faraday*).

Caoutchouc,	31·70	per cent.
Albumin,	1·90	,,
Bitter, nitrogenous substance, soluble in alcohol and water,	7·13	,,
Bitter, nitrogenous substance, soluble in water, insoluble in alcohol,	2·90	,,
Wax,	traces.	
Water and traces of acids,	56·37	,,

It must be mentioned that Faraday's analysis was made with a latex which had been imported into Europe, and consequently had considerable opportunity of undergoing changes in transit.

HEVEA (*Semmler*).

Caoutchouc,	32	per cent.
Water,	56	,,
Other organic and mineral substances,	12	,,

HEVEA (*Clouth*).

Caoutchouc,	32	per cent.
Organic nitrogenous substances,	2·30	,,
Mineral salts,	9·70	,,
Other mineral substances,	traces.	
Water,	55 to 56	,,

EUPHORBIAS RESINIFERA and CATTIMANDOO (*Henke*).

Euphorbene,	36·40	35	per cent.
Resins, soluble in ether,	26·95	27·40	,,
,, insoluble ,,	14·25	13·70	,,
Caoutchouc,	1·10	1·50	,,
Gum and salts precipitated by alcohol,	8·10	7·60	,,
,, ,, not ,, ,,	12·19	12·15	,,
Organic substances soluble in ammonia,	1·20	1·50	,,

The *Euphorbia* latices must be regarded rather as resin-latices containing a little rubber than as true rubber latices.

FICUS ELASTICA (*Adriani*).

Water,	82·3	per cent.
Caoutchouc,	9·57	,,
Resins, soluble in alcohol, insoluble in ether,	1·58	,,
Magnesia, combined with an organic acid,	4·49	,,
Substance, soluble in water and alcohol, insoluble in ether,	0·36	,,
Substance, giving a yellow solution with water; salts of calcium,	2·18	,,

Adriani's experiments were carried out with fresh latex, obtained from Sicilian or Indian *Ficus* trees.

HEVEA, from Amazon Delta.

Water,	47	per cent.
Caoutchouc,	32	,,
Mineral salts,	9·7	,,
Albuminoids,	2·3	,,
Resins,	9	,,

HEVEA, from Brazilian Plantations (*Seeligmann*).

Water,	55·6	per cent.
Caoutchouc,	32	,,
Resins, soluble in acetone,	traces.	
Albuminoids,	2·30	,,
Mineral matter,	9·7	,,

HEVEA, from Ceylon Plantations (*Parkin*).

Water,	55·14	per cent.
Caoutchouc,	41·27	,,
Sugars,	0·36	,,
Albuminoids,	2·8	,,
Mineral matter,	0·4	,,

HEVEA, from Ceylon Plantations (*Bamber*).

Water,	55·15	per cent.
Caoutchouc,	41·29	,,
Resins, soluble in acetone,	2·03	,,
Sugars,	0·36	,,
Albuminoids,	2·18	,,
Mineral matter,	0·41	,,

HEVEA, from Tonkin (*Vernet*).

Water,	54·38	per cent.
Caoutchouc,	37·91	,,
Resins, soluble in acetone,	0·62	,,
Sugars,	1·43	,,
Albuminoids,	2·30	,,
Mineral matter,	3·35	,,
Diastases,	traces.	
Sulphates,	0·01	,,

These analyses are of very considerable interest, for they show that, besides caoutchouc and water, its most important constituents, latex contains a variety of other substances, which are probably the residues of the substances from which it is formed; from these valuable information may be gathered as to the genesis of rubber. We shall probably find on studying these substances that they provide us with a good number of arguments in support of the theories of formation which we have already outlined.

Latex contains, then, sugars, resins, protein, acids, and caoutchouc, and we propose to consider each of these classes of substance in turn.

Carbohydrates of the Latex.—First of all, we have the starchy substances, sugars and glucosides, which have been already mentioned when considering the formation of rubber in the plant.

Weber,[1] from whom we can always find something to quote in connection with researches on the genesis of rubber, has laid down as a principle that the hydrocarbon is derived either from cellulose or, better still, from starch. His opinion was based upon the following:—The oxygenated compound —$C_{30}H_{48}$, $10H_2O$—which is found in Para rubber, must be regarded as a hydrate of "polyprene," and this hydrate can be none other than an intermediate product between cellulose and rubber.

Harries, for his part, regards rubber as being derived from pentoses.

These hypotheses are very tenable, more especially since Cross, when studying *Manihot*, found, as already mentioned, certain tubercles attached to the roots resembling those of the potato, and, like them, filled with starch; and since Dippel found little spindle-shaped grains of a very peculiar starch in the latex of *Euphorbia splendens*.

Harries' work, which has demonstrated the possibility of transforming rubber by ozonisation into levulinic acid, a substance which is easily obtained by the action of hydrochloric acid on starch, gives still further reason for thinking that rubber is derived from the carbohydrates in the plant. This is again the view held by Ditmar, who admits that it is likely that rubber may be produced by the action of the sugars which are often found in plants. He, therefore, regards the study of the carbohydrates found in latex as of great importance.

If rubber be a dimethyloctadiene—that is to say, a multiple of the radicle C_5H_8—it has some resemblance to cellulose and starch, which are polyanhydrides of grape sugar. Harries believes, as already stated, that it is the pentoses in particular which are active in the plant; that these are reduced to C_5H_8, which then condenses to $C_{10}H_{16}$.

These pentoses ought to be found in quantity in the laticiferous vessels, but neither Harries, nor Ditmar, nor other analysts have ever found any. On the other hand, they have isolated *inositol*.

Approaching the subject from another side, the synthetic preparation of a homologue of rubber has been realised, starting from erythritol, prepared from erythrene; this synthesis shows again that the sugars can be regarded, at present, as forerunners of rubber; their presence in the latex is, therefore, quite natural.

The study of these constituents of the serum has been carried to considerable length by Aimé Girard, and his work on *dambose* and *dambonite*, extracted from N'Dambo rubber, must be quoted.

Working with freshly imported latex, or with serum imprisoned in recently prepared blocks of rubber, Girard found in them peculiar substances, which behaved, from the chemical point of view, as true sugars.

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[1] J.S.C.I., 1900, 19, 215.

When carefully evaporated to dryness these latices gave coloured masses, from which colourless crystals of *dambonite* were to be obtained by extraction with alcohol.

Girard's description of *dambonite* is as follows :—" It is a white crystalline substance readily soluble in water, and in ordinary alcohol, but only sparingly in absolute alcohol. It melts at 190° C. and volatilises at 200° to 210° in the form of long, shiny needles. Its empirical formula is $C_4H_8O_3$. In presence of water it becomes hydrated, taking up three molecules, which it loses again at 100° C. The crystals of the hydrated substance are elongated prisms, with considerable tendency to twinning.

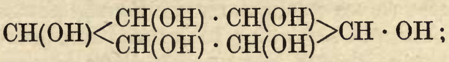
" *Dambonite* does not reduce Fehling's solution and does not undergo either alcoholic or lactic fermentation. It is attacked by concentrated acids, even in the cold, and at higher temperatures their action is more energetic ; with fuming hydriodic or hydrochloric acid at 100° C. action is complete in half an hour, and results in a remarkable hydrolysis. If the operation be carried out in a closed vessel, methyl iodide or chloride can be seen to form in the liquid, and in solution is to be found a new neutral substance with a sweet taste, non-volatile, crystallising well, and having the composition of a dehydrated glucose. This substance is *dambose*, and its production indicates the true constitution of *dambonite*, which must not be regarded as a polyhydric alcohol, like most sugars, but as a methyl ether, susceptible of hydrolysis. Latex thus contains a volatile, sugar-like substance, which differs both in composition and in chemical behaviour from the substances hitherto studied. This substance, *dambonite*, may be regarded as the methyl ether of another sugar-like substance, *dambose*, and the latter, remarkable for its great stability, evidently belongs to the glucose family, and is perhaps able, like the other members of that family, to function as a polyhydric alcohol."

In the course of investigations carried on between 1871 and 1873, Girard succeeded in isolating *Bornesite* from the latex of *Urceola* (Malay), and *Matezite* from certain Madagascar latices ; these two compounds are methyl ethers of *Borneo-dambose* and *Matezo-dambose* respectively. Girard was able to recognise distinctly, on comparing them, that the three *damboses*, formed by hydrolysis with mineral acids, were not identical ; he was able to determine relationships between their physical properties, which, in conjunction with their chief chemical properties, give reason for regarding them as the results of progressive condensation of one and the same compound —$C_4H_8O_3$.

The composition and properties of the six substances are summarised in the following table :—

		Melting Point.	Rotatory Power.
		° C.	° C.
Dambonite, .	$C_8H_{16}O_6$,	205	± 0
Bornesite, . .	$C_7H_{14}O_6$,	200	+32
Matezite, . .	$C_{10}H_{20}O_9$,	181	+79
Dambose, . .	$C_6H_{12}O_6$,	212	± 0
Borneo-dambose,	$C_6H_{12}O_6$,	220	± 0
Matezo-dambose,	$C_9H_{12}O_9$,	235	+ 6

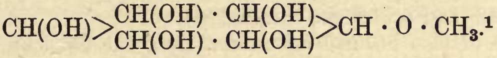
The constitution of *dambose* is represented by the formula—



$$\mathrm{CH(OH)} < \begin{matrix}\mathrm{CH(OH)\cdot CH(OH)}\\ \mathrm{CH(OH)\cdot CH(OH)}\end{matrix} > \mathrm{CH\cdot OH};$$

dambonite is the corresponding dimethyl ether, $C_6H_6(OH)_4(OCH_3)_2$.

Borneo-dambose is identical with inactive *inositol*, and *bornesite* its monomethyl ether,



$$\mathrm{CH(OH)} > \begin{matrix}\mathrm{CH(OH)\cdot CH(OH)}\\ \mathrm{CH(OH)\cdot CH(OH)}\end{matrix} > \mathrm{CH\cdot O\cdot CH_3}.$$[1]

For a long time it was thought that only the latex of *lianas* contained sugars, and it was thought that on that fact might be based a method of differentiating between rubber from such sources, and that derived from trees. Further investigation showed, however, that this supposition, which had been defended by Seeligmann, could not be confirmed. Weber, in fact, obtained on concentrating serum prepared by centrifuging *Castilloa* latex, a yellow, friable amorphous mass. This product consisted of various substances, including mineral salts, which we shall consider in a moment, and a compound which gives, as we have already said, a voluminous greenish-black precipitate with ferric chloride.

From this compound two crystalline substances are obtained by acid hydrolysis; one, melting at 195° C. and subliming at 200° to 210° C., is Girard's *dambonite;* the other, crystallising in fine needles, is insoluble in water, and appears to be a derivative of *coumarin,* allied to *aesculin* Hence *Castilloa,* which is a tree, gives a latex containing a glucoside, like the *lianas.*

This substance has also been met with by *Young* in Amazonian *Hevea Braziliensis* latex, in company with various other hydrocarbons. On referring to the analyses of latex on pp. 91 and 92, it will be seen that glucosides, in quantities varying from 0·3 to 4·17 per cent., have been found by Parkin, Bamber, Scott, and Vernet in *Hevea* latex.

Lastly, in 1911, Pickles and Whitfield, made an interesting communication on the amount of glucosides contained in plantation rubber from Singapore and Ceylon. On examining the acetone which had been used for extracting the resins from certain samples, at the Imperial Institute, London, they found in it a considerable quantity of a crystalline substance, soluble in hot water, and representing about 2 per cent. of the dry rubber; they identified this substance as *l*-methylinositol. When these experiments were repeated on the original latex the presence of *dambonite,* to the extent of 0·5 per cent., was confirmed.

The presence in latex from all sources, and of every kind, of particular glucosides, belonging to the *inositol* group, is, therefore, now firmly established, and up to a certain point the belief is justified that they form the residues of a material which has served for the elaboration of rubber.

Acids and Salts in the Latex.—The acidity of latex is, as a rule, very slight. Vernet estimates it at 0·01 per cent., calculated as H_2SO_4; as a matter of fact only traces too small for determination are to be found in it of various fatty acids, and a special acid, which has been detected by Adriani, but has not been isolated.

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[1] Flint and Tollens found yellow crystals of methylinositol in the rubber wash-water at a factory in Hanover.

There are only small quantities of mineral salts present also, consisting of magnesium salts (more particularly in *Ficus*), potassium, calcium, and sodium salts (in *Hevea*). According to Adriani the potassium, sodium, and calcium salts of the particular acid discovered by him in latex are insoluble in water. Oxalates have been found in *Vahea gummifera*, and by way of exception these salts are present in quantities sufficiently large to have enabled Merellet to see crystals of them distinctly when sections of laticiferous vessels were examined under the microscope.

But in spite of this interesting observation, the content of mineral salts in the latex is so small, and their presence there is so natural, that no further time need be spent upon the subject.

Resins in the Latex.—By the term *rubber resins* is meant those constituents which can be separated from the serum by extraction with acetone or alcohol. Not a great deal is known about them.

The investigations of Terry, Tschirch, Bourne, Spence, Hinrichsen, Marcusson, Kindscher, Manasse, Kuster, and d'Oehler have determined their appearance, melting points, certain of their reactions, their rotatory powers, and their iodine values. Most of them are optically active, their activity residing mainly in the unsaponifiable portion; the latter often consists of secondary alcohols, analogous to cholesterol.

Since the resins are only present in rather small quantities in the latex, and are, as a rule, precipitated with the rubber on coagulation, their detailed study will be more appropriately undertaken when dealing with the analytical examination of the rubber.

Certain latices, such as those of *Almeidina*, the Congo *lianas*, and *Jelutong*, as well as of several Malaysian rubber trees, contain more resin than rubber. From the point of view of exploitation it would be more advantageous to be able to extract these from the latex itself, rather than to precipitate them with the coagulated rubber, rendering the latter highly impure.

Protein in the Latex.—Latex, of whatever origin, contains appreciable quantities of proteins; according to Weber's analyses the proportion of these substances present is often as high at 7 per cent., when separated from the rubber by centrifugal action. This protein has the peculiar property, in the possession of which it differs considerably from ordinary protein, of becoming coagulated only very slowly and very incompletely when heated.

On the other hand, it coagulates very rapidly on the addition of acids, especially acetic acid. It is also precipitated by other ordinary precipitants of protein—alum, mercuric chloride, and hydroferrocyánic acid.

Since protein is present in the latex, it is improbable that tannins are also present, as suggested by certain authors, whose opinion has been based upon the colour-change exhibited by rubber latex on the addition of ferric chloride. We have seen that this reaction is really due to the presence of glucosides. The addition of tannin to the serum brings about immediate coagulation. Since most of the substances which react with protein are entirely without action on rubber, in order to account for the precipitation of the latter by them, it is necessary to assume that the globules of rubber are surrounded by a thin pellicle of protein material. This is what Weber has demonstrated in his very important study on *Castilloa* latex, published in 1903,[1] from which the following is quoted:—

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[1] *Ber.*, 1903, 36, 3108.

"All the precipitants of alkaloids, as well as the coagulants of protein, react upon latex, without exception. One has, therefore, good grounds for attributing the coagulation of latex to the coagulation of the protein, which surrounds and carries down with it the suspended rubber globules. On the other hand, I have shown that rubber cream, which has been separated from the serum by centrifugal action, and which forms a thick mass, very rich in rubber, is not coagulated by these reagents. Microscopic examination reveals an interesting fact; the globules floating in the serum are surrounded by an exceedingly thin pellicle of protein" (a fact which we have referred to already, and which was known before Weber). "But, more curious still, the contents of these ovule-like bodies are not ready-formed rubber, but rather an *oily substance*, as had already been seen by Preyer. It had seemed to me paradoxical that rubber, with its physical and chemical properties, could exist as such in the more or less mobile liquid—more often than not very fluid—which flows from the incisions in the producing plant. If these globules be crushed beneath the cover glass, they burst and allow their contents to escape; on contact with the air the latter coagulate pretty rapidly. Polymerisation, which is the immediate result of this coagulation, seems in such a case to be determined by a two-fold influence, mechanical and chemical, the latter due to oxidation. That the mechanical cause seems to be of predominant importance is shown by the following experiment:—When latex diluted with five times its own volume of water, is allowed to stand for 24 hours, a creamy layer forms on the surface. This can readily be separated from the serum. If the cream thus separated be beaten, or 'whipped,' for a short time, it becomes pasty, and is then in a condition to be worked on a small pair of mixing rolls. At the beginning of this operation the pasty mass passes through the rolls, in the same way as would an ordinary bread dough, without offering any resistance. It can be removed from the surface of the rolls by the hand without the least effort, and the sheet thus obtained has no strength, breaking under its own weight. On prolonging the time of mastication a moment arrives when the two rolls tend to separate, being forced apart by the resistance of the paste, which has suddenly become firm and elastic; pressure is exerted on the bearings, and as the mass passes through the rolls the peculiar noise characteristic of the process of masticating rubber is produced. The mass gets warm, and, under the influence of the heat produced, polymerisation becomes more marked, and results in the production of an actual lacework of pure rubber."

The conclusion which it would appear can be drawn from this preliminary experiment is that elastic rubber does not pre-exist in the latex, but that the substance is present there in the form of an intermediate product, dimethyloctadiene or a polymeride of that hydrocarbon. The further investigations made by Weber confirm this hypothesis.

"The experimental verification of such an hypothesis," he says, "offers the greatest scientific and technical interest. How then to proceed? The most practical method, to this end, consists in agitating latex with ether."

Contrary to the views held by many authors, beginning with Macquer and Hérissant, Weber maintains that ethyl ether does not dissolve a trace of pure rubber. We shall examine this point later on.

If, therefore, the globules of latex contain rubber ready-formed, agitation with ether will not effect a separation of the globules from the emulsion; if, on the contrary, the globules contain some ethenoid terpene, capable of polymerisation to rubber, one would expect to see this compound dissolve in the ether and thus become separated from the serum.

Weber says, " I carried out the experiment by shaking up about a litre of latex with excess of ether in a large separating funnel. I had the satisfaction of seeing, at the end of a few seconds, the liquid clear and the ether rise very rapidly to the surface of a perfectly limpid aqueous layer.

" I ran off the latter, and left the ethereal solution in the dark for twenty-four hours, in contact with anhydrous sodium sulphate to dry it, and on the following day it was filtered. The ethereal solution thus obtained is colourless, and very fluid ; it closely resembles a solution of terpenic compounds in ether. On evaporation it yielded 28 per cent. of a thick oil, which solidified rapidly, especially when exposed to light.

" In this way a rubber is obtained which is absolutely insoluble in ether, but soluble in benzine and all the ordinary solvents of rubber.

" When it is remembered that all solutions of pure Para of 20 per cent. strength form thick jellies, it will be seen that there can be no doubt about the conclusions to be drawn from this experiment.

" The ethereal extract of the latex does not contain rubber in the true sense of the word. It contains an intermediate substance, very soluble in ether, like the olefinic compounds, solutions containing 43 per cent. of the substance being still fluid. Subsequently, when the ether evaporates, and under the influence of light, the substance is transformed into rubber.

" Such solutions can be preserved for a short time without visible change, if kept in a cool place and in the dark, but not indefinitely. After a time it will be noticed that the liquid thickens. Polymerisation, once it is started, proceeds very rapidly, and in two days the fluid solution is transformed into a colourless jelly, remarkably solid and resistant. If the containing vessel be broken, and the jelly be allowed to lose its ether by evaporation at ordinary temperature, it becomes horny, changing into a vitreous mass, fairly transparent, yellow, elastic, and tough, in short possessing in a high degree all the properties of good rubber."

Later on, certain facts, which were first brought to light by Macquer in 1768, and published by Faujas de St. Fond in 1784,[1] were rediscovered independently by Weber, who observed that the use of aqueous ether, which had been already employed by Winch (2 parts of water to 1 of ether by volume) facilitates polymerisation.

Weber says :—" I have noticed that polymerisation is more or less rapid according to the proportion of water contained in the ether employed. With the driest ether which I was able to obtain, the rubber-forming terpene will remain in the liquid state, with no sign of solidification for five weeks."

This fact, which defines the rôle of aqueous ether in the process of polymerisation, should be remembered ; for, from the technical point of view, it should permit of the absolute condensation of the products of synthesis by treatment subsequent to the condensation or polymerisation by heat, and should also allow of the improvement of viscous natural rubbers and of sticky reclaimed rubbers.

" The ethereal solution of the parent terpene shows no sign of any change when boiled for six hours in a vessel fitted with a reflux condenser. The addition of a drop of hydrochloric acid brings about, in a few seconds, tumultuous, almost explosive ebullition ; in a few moments the liquid is

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[1] *Histoire de l'Académie des Sciences,* 1768, p. 210.

transformed into a spongy mass, the temperature of which, at the moment of coagulation, is about 61° C. The cavities of the sponge thus obtained are at first swollen with ether, but they soon collapse, and, when the ether has evaporated, the product resembles very closely that formed on spontaneous polymerisation.

"When extracted with acetone, these rubbers gave about 3 per cent. of a resin which differs from that contained in normal rubbers, only by its almost white colour. It seems clear that this resin pre-existed in the rubber-forming terpene, and was enveloped in the mass on coagulation. It, therefore, appears to be an impurity, a product present when the transformation into rubber takes place, and not formed by a parallel reaction.

"The acetone-extracted rubber gave the following analysis :—

Carbon, ...	87·89 per cent.
Hydrogen, ...	11·80 ,,

The figures obtained for purified Para rubber being :—

Carbon, ...	87·27 per cent.
Hydrogen, ...	12·73 ,, "

From this very interesting study of Weber's, which marks a very definite epoch in rubber research, it follows undeniably that rubber does not exist ready-formed in the latex. It is formed, subsequently, by the polymerisation of an unsaturated terpene-like compound having the appearance of a fairly fluid oil, subdivided into minute globules, each of which is surrounded by a thin envelope of protein ; suspended in the serum these globules constitute an emulsion. The latex, therefore, contains only an intermediate product.

It is true that the whole of the foregoing explanation relates only to *Castilloa* latex, but it is probable that Weber's observations are applicable to many latices.

It is to be regretted, from every point of view, that a method of investigation so clear and practical as that instituted by Weber has not been applied, with the substitution for ether of a solvent for terpenes, to the different latices to be obtained from trees, lianas, herbaceous plants, and rhizomes. It should have been possible thus to make a considerable advance in the chemistry of rubber, and most likely to have gained precise knowledge of the mechanism by which the parent terpene is formed in the plant.[1]

It is equally to be regretted that when Weber had this body in his hands he did not, in spite of all the delicacy of the research, pursue the study of it further.

Is this singular compound "*Viscine,*" the peculiar terpene discovered by Parkin, Esenbeck, and Marquart in the branches and leaves of rubber trees, and which, according to them, is polymerised in successive stages during ten years into rubber ? Or is it dimethyl-*cyclo*-octadiene, Harries' hypothetical compound, the existence of which in nature would thus confirm the many theories which have been developed around it ?

On this subject there is room for any hypothesis.

We have just seen that the latices of nearly all rubber plants contain protein substances, similar to other proteins of animal and vegetable origin.

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[1] Weber's method was applied to the latex of *Mascarenhasia anceps* by Jumelle; with ether immediate coagulation occurred, a spongy mass, turning chocolate colour on drying, being produced. Tannin, mercuric chloride, and other protein precipitants are without action on this latex.

Like the resins, these are retained by the rubber up to the moment of coagulation. Although great importance has been attached to them from the point of view of the quality and stability of the commercial product, little attention seems to have been devoted to them, apart from the work of Spence.[1] Weber pointed out their presence in his long study of *Castilloa*, but his analysis was not extended to them.

It is these bodies, however, which appear to constitute, in the coagulated rubber, what is called the "insoluble constituent"—viz., that portion which can be isolated by dissolving the remainder in chloroform, and washing the residue repeatedly with that solvent. This constituent was studied by Weber, Fendler, and Dumas, but all of these workers failed to recognise its nitrogeneous character. We shall refer to their work again shortly. According to Spence, this protein, when freed from rubber, forms a brown, friable mass, devoid of elasticity; it does not swell up in contact with solvents, it shows the xanthoproteic reaction with nitric acid, but does not react with Millon's reagent. Its fairly considerable ash consists of lime and iron oxide, similar to that of fibrin and casein. Its nitrogen content varies from 1·9 to 4·2 per cent., the latter figure corresponding to 33 per cent. of actual protein, assuming that the latter is of similar composition to most proteins, which contain about 15 per cent. of nitrogen. It is very likely a substance closely related to the glyco-proteins.

We have already seen that when latex is left for some twenty-four hours exposed to the air, it turns brown fairly rapidly, and is gradually converted into a kind of black tar. This change was generally attributed to the presence of oxidases, although it did not even appear to be necessary to demonstrate their existence experimentally.

In Czapek's view,[2] oxidase is only a partial cause of the change of colour; Weber,[3] as we have already seen, attributes the darkening of the latex to oxidising enzymes, and Tschirch[4] shares this opinion. Schidrowitz and Kaye[5] have endeavoured, unsuccessfully, to characterise these enzymes.

Spence,[6] dealing with fresh *Funtumia* latex, has succeeded in extracting from it peroxidases, and his work is of the greatest interest from the biological point of view.

By diluting the latex so as to cause the globules to separate from the serum in virtue of their lower density, washing the globules and uniting the wash waters with the serum, Spence obtained a liquid lending itself to examination for oxidase. After filtration this extract is alkaline to litmus and gives Millon's reaction, although in an uncertain fashion. It is purified by dialysis, and its behaviour is then that of a peroxidase—that is to say, of an indirect oxidase, one which reacts only in the presence of hydrogen peroxide with tincture of guaiacum, *ortho*-phenylenediamine, phenolphthalein, amidol, or pyrogallol.

Spence claims to have been able to identify, in the course of his experiments, not only a peroxidase, but also a catalase, which liberates oxygen from hydrogen peroxide.

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[1] *J. Inst. Comm. Research in Tropics*, 1908, 3, No. 6.
[2] *Biochemie der Pflanzen*, 1908, II, 705.
[3] *Ber.*, 1903, 36, 3110.
[4] *Die Harze und Harzbehälter*, 1908, 992.
[5] *India Rubber Journal*, 1907, 34, 24
[6] *Biochemical Journal*, 1908, 3, 351-352.

A much more active peroxidase is obtained when alcohol is substituted for water in the extraction process.

From the chemical point of view, although the peroxidase contains nitrogen, it is not a protein. When fused with potash it gives the pyrrol reaction, and with phloroglucinol and hydrochloric acid it reacts as a pentose.

According to Vernet and Wildemann the latex in the tree is a product of its physiological activity and serves as food; it is a material which is being continually elaborated and continually utilised in the life activity of the plant.

The function of the oxidases, on this assumption, would be to convert the material of the globules into a simpler form, similar perhaps to the levulinic acid or aldehyde which Harries obtained by the hydrolysis of the products of ozonisation of rubber.

Under these circumstances the conclusion may be drawn, up to a certain point, that the peroxidases bring about the transformation of rubber into oxidation products which can be utilised by the plant, and it is also conceivable—and this would constitute an important fact in connection with the study of the formation of rubber in the plant—that the inverse reaction may also be facilitated by the oxidases, the oxidation product of the rubber playing the part of hydrogen peroxide in presence of them. If, for the moment, Spence's views be adopted, it will be seen that with the aid of the oxidases it is easily possible to pass from rubber to levulinic acid, and, as has been shown by Weil,[1] in the reverse sense from levulinic acid to rubber.

Such a reaction may be of enormous importance from the point of view of a synthesis, if the peroxidase which brings it about can be isolated; for levulinic acid is easily obtained by the action of hydrochloric acid on starchy substances. We shall have occasion to return to this synthesis elsewhere.

Spence, pursuing his studies on the nitrogenous compounds found in latex, has determined, as already stated, that the whole of the nitrogen is not present in the form of protein, because the amount of insoluble impurities is much less than that calculated from the nitrogen content. Crystalline nitrogen-containing compounds are to be obtained from latex, which has undergone fermentation and afterwards been dialysed. Under ordinary circumstances these compounds remain in the serum and are not found in the coagulum. Thus Spence found that a serum contained 0·15 per cent. of "crystalloid" nitrogen, which is not coagulated by heat, nor by nitric acid.

The dried dialysate was insoluble in benzene and chloroform, and partly soluble in acetone; when heated it gave off an odour of caramel before being converted into carbon. The aqueous solution reduced Fehling's solution, and with silver nitrate gave, in the cold, a white precipitate, and when warmed a silver mirror.

Three successive dialyses of the same sample gave of crystalloid products—total solids in the dialysate 1·57 per cent., which could be separated into organic crystalloids—sugars and organic acids—1·4 per cent.; and inorganic crystalloids 0·206 per cent. In other samples Spence found as much as 3·5 per cent. of organic crystalloids.

The bases of the inorganic portion were chiefly potash and magnesia, the latter in the smaller quantity. Neither iron nor calcium was found.[2]

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[1] Lecture at Vienna

[2] *J. Inst of Comm. Research in the Tropics.*

CHAPTER VII.

COAGULATION.

Before passing from the study of the physical and chemical properties of latex to the examination of rubber, properly so called, it is necessary to study in the fullest detail the very important process of coagulation, the purpose of which is to separate the rubber from the serum. The manner in which this exceedingly delicate operation is conducted determines, in large measure, the commercial value of the product; this is sufficient to indicate its importance.

On account of the colloidal character of rubber, its coagulation raises a number of problems which do not yet appear to be completely solved, in spite of the large amount of study devoted to them. The reason for this is that the question is as much a physical as a chemical one, and that our knowledge of the colloidal state is still rather limited.

It seems clear—as Vernet remarks[1]—that if we wish to isolate from so complex a substance as latex the rubber which it contains, in a condition of great purity and in a single operation, it is essential that the method employed should bring about the coagulation of the rubber only, and should leave the other constituents of the latex in solution. Unfortunately, at the present moment there exists no practical method which enables us to do this by any process of chemical selection. All the known crude rubbers, including the highest grades, such as *fine Para*, contain after being washed and dried impurities derived from the serum, of which the chief are resins, proteins, and mineral substances.

All methods of coagulation do not act in the same way—in a qualitative or in a quantitative sense—upon these secondary constituents of the latex. If, for example, the serum from an acetic acid coagulation be examined, it will be found that after filtration a considerable amount of protein is precipitated on the addition of alcohol, or by heating, whilst the rubber itself, obtained from the same latex, also contains a certain amount.

The same is true of the resins; part of them is precipitated with the rubber, whilst another portion remains in the serum.

In order to arrive at a method of completely eliminating these secondary products from the rubber, or at any rate of reducing to a minimum the quantity precipitated with it, much work will be necessary, and it has scarcely been begun.

The choice of coagulants, the proportions of their various constituents, the amount of them to be used in relation to the amount of latex dealt with, to the character of the serum, and to the rubber-content of the latex, are points not clearly determined.

It will only be as the result of very lengthy experiments that the best conditions under which to employ coagulants will be determined, and until this is done we shall be working somewhat in the dark.

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[1] *Le Caoutchouc et la Guttapercha*, 1911, 8, 5689.

Rubber can also be extracted from the latex containing it by simple desiccation, instead of by the use of coagulants. In that case a dry extract is obtained which can no longer be completely taken up by water to reform the original latex. Such an extract will obviously contain all the non-volatile substances, the presence of which in the latex has been revealed by analysis, and it is of necessity impure. Rubber prepared by smoking—*Sernamby* for example—is, however, obtained in this way, and is highly esteemed in quality.

If the latex be acid, either naturally, as the result of fermentation, or artificially, by the addition of mineral or organic acids, coagulation can be brought about by boiling. The latex thickens at 65° C., and begins to coagulate at 70° C.; but the method is not to be recommended. If the heating be carried out over a naked flame local superheating occurs, and at these points the rubber suffers in quality; if steam be employed, either live or in a jacketed pan, coagulation is always imperfect because of the low conductivity of rubber, and some of the latter always remains in the serum.

Leaving out of account these purely thermal methods of coagulation, it can be said that up to the present two chief theories have been put forward to explain the phenomena of the separation of solid rubber from the liquid serum.

One of these was formulated, some time ago, by Weber, and it allots to the proteins contained in the latex the chief rôle in the process. These are rendered insoluble, by appropriate reagents, and this brings about the precipitation of the globules of rubber and the formation of a clot, in the same way as the globules of hæmatin in the blood are agglutinated by the coagulation of the blood albumen.

The other theory is due to Victor Henri, and, based upon a series of physico-chemical and electrolytic observations, likens coagulation to the precipitation of colloids. In this case the determining cause is supposed to be an electrolyte, salt, acid or alcohol, or a mixture of these.

We shall consider these two theories in succession; but it will be well, before proceeding to do so, to summarise the principal characteristics of colloids, since we shall frequently have to make application of their peculiar properties.

Properties of Colloids.—The colloids, first recognised as a class by Graham, have been investigated in a general way by Grimaux, Van Bemmelen, Paal, Muller, Voit, Jordis, Colson, and Fouard, and, from the special point of view of rubber, by Weber and de Fleury; the latter has published an illuminating *résumé* of their properties in *Le Caoutchouc et la Guttapercha,* of December, 1911, and from this article we shall quote a number of extracts.

The colloids are amorphous, non-crystallisable substances, forming in the dry state horny masses, more or less translucent, or taking the form of gelatinous masses.

Some, like albumin and gelatin, are soluble; others, like fibrin, gum tragacanth, and rubber swell up in various liquids without dissolving completely in them.

The coagulation of these bodies, their separation from solution in an insoluble gelatinous form, or *gel,* often occurs as the result of almost inappreciable influences. They then pass, in Graham's language, into the *pectous* state.

Graham says: "The existence of colloids is nothing but a continual metamorphosis, and the colloidal state is rather a dynamic condition of matter, the crystalline state being its static condition."

It is to-day held that matter is not divisible *ad infinitum*, not, at all events, without destruction or transformation of the chemical species which it represents. Each of these chemical species has its own limit of divisibility, to which the name of "*molecule*" has been given, whilst the name of "*atom*" is reserved for the smallest quantity of a simple substance which enters into the composition of a molecule. The term "*molecular weight*" is applied to that weight of a given substance which in the gaseous state occupies the same volume as 2 grammes of hydrogen—viz., 22·4 litres. Since all substances cannot be vaporised, various methods, such as the ebullioscopic, the cryoscopic, and the osmotic pressure methods, are employed in the determination of their molecular weights.

The molecule of a colloidal compound may be much more complex than an ordinary molecule, and may be made up of a multiple assemblage of molecules, of the same percentage composition. The substance is then said to be a polymeride of the one with the simple molecule, which is called the *fundamental molecule.*

This is the case with rubber, which is made up of an assemblage of an unknown number of fundamental molecules, $C_{10}H_{16}$. Certain thin membranes are permeable by certain salt solutions, whilst remaining impermeable by other dissolved substances. This form of filtration, known as *dialysis*, renders possible the separation of crystalloid bodies, which pass through the membrane, from colloidal bodies which do not traverse it.

Rubber latex and rubber solutions possess the properties of colloidal compounds, and cannot be *dialysed.*

It is assumed that the molecules of a dissolved substance are diffused through the solvent, in the same manner as gaseous molecules in a closed space. Mariotte's law, and the Avogadro-Ampère hypothesis, are applicable to them, and it follows that if the solutions be contained in a closed space, a pressure is exerted by them against the surrounding walls, proportional to the number of molecules. A dissolved substance tends to occupy, with an expansive force which is measurable, the whole volume of solvent offered to it. This expansive force, which, under certain conditions, shows itself as a pressure, is called *osmotic pressure;* it is proportional to the number of molecules contained in a given volume. It will, therefore, be seen that the osmotic pressure may afford a measure of the molecular weight and of the relative sizes of molecules in the dissolved state.

On applying the method of dialysis, it is obvious that substances with small molecules, which consequently pass easily through the membrane, ought to give considerable osmotic pressures; this is the case with crystalloids. On the other hand, substances with very large and complex molecules, which do not easily traverse the membrane, ought to give very small osmotic pressures; that is the case with colloids in which the number of molecules per unit of mass is relatively very small.

Whereas the physical "constants" which serve to distinguish substances from one another, such as melting point, solubility, etc., are true constants in the case of crystalloids, they have no degree of constancy in the case of colloids.

This indeterminacy is to be explained by the perpetual change going on in the equilibrium between the assemblages of molecules, under the influence of the simplest causes, and of extremely weak internal forces. The *micellæ,* which represent the limiting physical state of division of colloids, become more or less complex, from moment to moment, under the most diverse influences.

As regards the physical properties of colloidal compounds, the molecular condition seems to play a more important part than the chemical species of which they are made up.

Simple contact action often suffices to bring about a particular condition of the compound, as a kind of inductive effect, without any chemical change being discernible on analysis.

The character of the solutions formed by rubber, and its behaviour on dialysis, lead to its being definitely classed amongst substances with very large molecules.

The term crystalloid is applied to a crystallisable substance, the molecule of which is of comparatively simple build.

The term colloid is applied to non-crystallisable substances with very large molecules, consisting of assemblages of numerous other molecules, either of different species or of the same species. In the latter case the compound is said to be polymerised; this is the case with rubber, which is a polymeride of the fundamental molecule, $C_{10}H_{16}$.

It is obvious that since the passage from simple to complex chemical compounds is continuous, no very definite line of demarcation between the crystalloidal and the colloidal state can be drawn. It is thus possible to grasp the full truth of Graham's phrase, which has just been quoted.

Nevertheless, the distinctly colloidal state is evidenced by the existence of a number of characteristic properties, chief amongst which is *variability.*

These modifications take place in rubber, the molecules of which are electro-negative, and which is agglutinated, for example, under the influence of electro-positive bodies in very small quantity.

A colloidal compound may induce a similar physical state in other bodies; coagulation of latex in the presence of freshly coagulated rubber is an example of this.

Under the influence of certain reagents the physical properties of colloids are susceptible of modification; this is the case with Para rubber, which, when it has been precipitated from solution and dried, is less soluble in benzine, but which recovers its solubility on heating with boiling acetic acid. Here, in the first case, there has evidently occurred a kind of superpolymerisation, and in the second case a depolymerisation. There has, therefore, been some change in the molecular complex, and this evidences itself also when viscosity measurements are made; yet the elementary chemical composition is not affected, and can still be represented by the formula $C_{10}H_{16}$.

Changes of temperature, as well as the action of light, bring about modifications of a similar kind. Minute traces of certain reagents are sometimes sufficient to bring about polymerisation, as in the case of the action of metallic sodium in the conversion of isoprene into synthetic rubber. Rubber, then, by reason of its colloidal nature—its molecule being a complex formed by the union of several fundamental molecules—is in a condition of continuous flux, passing from one degree of polymerisation to another; the internal equilibrium is undergoing continual modification under the influence of little known causes. In this sense the description of rubber as a "living substance" can well be justified.

Colloidal solutions are designated *sols.* The name of the solvent is sometimes prefixed—*e.g.*, *hydrosol*, *benzenosol.* All the properties of these solutions are the result of the great size and complexity of the *micellæ.* Examination by the ultramicroscope reveals the presence of suspended particles in the solutions, and these particles are in a state of constant oscillation, known as Brownian movement. The boiling and freezing points of these solutions differ very little from those of the pure solvents, and it is thus practically impossible to apply the ebullioscopic or the cryscopic method to the determination of the molecular weight of the dissolved substance. The osmotic pressure is excessively low, and can only be measured with difficulty. This low degree of osmotic activity is due of the character of the colloidal suspension, which is displayed by the passage of a beam of light through a colloidal solution. The beam becomes diffused and polarised, as when fine particles are suspended in a liquid.

It is to be noted that in solution, whether in benzene or in chloroform, rubber behaves towards certain reagents—such as bromine, nitrous acid, and ozone—as though it were made up of a single fundamental hydrocarbon molecule, $C_{10}H_{16}$, the reacting unit being, as Weber rightly states, the smallest molecular unit. In such cases a preliminary depolymerisation is brought about either in the process of solution or by the action of the reagent, the result of which is to break down the complex into its free fundamental units.

In vulcanisation, on the contrary, the sulphur, according to Weber, has a pectising effect upon the non-depolymerised complex. Sulphur and perhaps chlorine seem to be the only two substances at present known which are capable of stabilising the rubber hydrocarbon complex, and of arresting the perpetual changes in degree of polymerisation.

Theories of Weber and Harries.—Two of the best qualified workers on the subject of rubber, Weber and Harries, have set forth their views upon the colloidal nature of rubber, Weber in his "Theory of Vulcanisation," and Harries in his lecture in Vienna on the synthesis of rubber.

The following is a summary of their general ideas which are often very suggestive :—

"All the properties of colloids," says Weber, properties of which an account has just been given, "afford evidence, without exception, of the characteristically very great size of colloid molecules, but none of these properties provide us with the means of distinguishing sharply between the colloidal and the crystalloidal state."

From this it follows : either that the colloidal state is simply a function of the molecular weight and does not differ essentially from the crystalloidal state ; or that it is the result of the conjunction of several physical and perhaps chemical properties.

Does not the fact that, although produced in a normal way by the interaction of silver nitrate and sodium chloride, silver chloride is not precipitated in the presence of a concentrated colloidal solution, but remains in solution in the colloidal state, tend to the belief that colloids can, by induction, determine the colloidal state ? If caoutchouc can exist in the crystalloidal state, is not its usual colloidal state determined *inductively* by other portions of the polyprene in a partly colloidal state ?

When, from various causes, some physical and some chemical, colloids pass over into an insoluble form, they are said to form, as already explained, a *pectum*, and become *pectised* bodies. They are often called *gels*.

In Weber's view, the most important case of *pectisation* is that in which colloids pass into a state of chemical combination ; in that case it does not matter in the least whether the substance entering into combination with it be a colloid or a crystalloid; the compound produced will always be a colloid.

In such compounds two physical possibilities present themselves: either there is an aggregation of molecules, to form larger molecules—that is to say, polymerisation takes place—or the large molecules initially present become subdivided into smaller molecules, which, however, always retain a "colloidal" degree of aggregation. These ideas can be represented by the two following equations, which are symbols of the two hypotheses of pectisation:—

$$(1) \qquad m(C_{10}H_{16})_n + mX = (C_{10}H_{16})_{mn}X_m.$$

$$(2) \qquad (C_{10}H_{16})_n + nY = p\left\{(C_{10}H_{16})_{\frac{n}{p}}Y_{\frac{n}{p}}\right\}.$$

In these equations, $C_{10}H_{16}$ represents the fundamental molecule—dimethyl-*cyclo*-octadiene—of the rubber colloid, m and n are coefficients, X and Y are molecules of substances entering into combination with the rubber. Vulcanisation appears to be an example of the first case, whilst the second is represented by the formation of the tetrabromide and other halogen derivatives, and of the nitrosites and ozonides.

Weber explains his ideas by means of an example taken from vulcanisation. He says: "If to a solution of rubber we add chloride of sulphur, the latter combines quantitatively with the rubber—when the quantity of chloride present is not too small—and rapid pectisation ensues."

If there is an excess of sulphur chloride all the fundamental molecules are attacked, and transformed into $C_{10}H_{16}S_2Cl_2$ molecules. The modified "polyprene" derivative takes the form $(C_{10}H_{16}S_2Cl_2)_n$.

If there is only a small proportion of sulphur chloride, every fundamental molecule does not enter into combination, but only the polymerised "polyprene" molecule; an addition compound of the form $(C_{10}H_{16})_nS_2Cl_2$ is obtained. In the first case the reacting molecule is $C_{10}H_{16}$, in the second case $(C_{10}H_{16})_n$.

But in both cases a pectised substance is the result.

When bromine, chlorine, hydrogen chloride acid, or nitrous acid act upon rubber, the reaction takes a different course. When the quantity of bromine is small the compound produced is not, as in the preceding case, of the type $(C_{10}H_{16}Br)_n$, but of the type $C_{10}H_{16}Br_n$, the excess of rubber remaining in the free state as $(C_{10}H_{16})_n$. With these reagents rubber interacts as the fundamental molecule $C_{10}H_{16}$, and it would seem, therefore, that the primary result of their action is to depolymerise the rubber. With sulphur or sulphur chloride, on the contrary, rubber interacts as the polymerised $(C_{10}H_{16})_n$, functioning as a single molecule.

From this theory of its behaviour as a colloid, Weber deduced a complete principle of vulcanisation, which we quote here, although it is strictly speaking outside the scope of our subject:—

"Vulcanisation is only brought about by means of agents which can give rise to pectised derivatives of rubber"; that is to say insoluble compounds, whatever be the character, crystalloid or colloid, of the substance which brings about the change.

"Vulcanisation, then, whether by sulphur or sulphur chloride, is only a form of pectisation," and vulcanised rubber should, therefore, be appreciably insoluble.

"Rubber is a colloidal compound" says Harries, "and it is indeed one of those rare colloids which can be obtained in a comparatively pure state; this arises from the fact that it is soluble in solvents which, like benzene, do not contain water.

"Soluble in the nascent state in certain compounds, such as ether, it may become insoluble by the action of heat, and recover its solubility when treated with acetic acid. In the second case a superpolymerisation appears to take place, and in the third a depolymerisation."

If to a solution of rubber in benzene concentrated sulphuric acid be added, the rubber separates in the form of an insoluble, brittle mass, having no resemblance to ordinary rubber; superpolymerisation or pectisation has occurred.

The passage of coagulable colloids from the *sol* to the *gel* condition may be brought about by three different causes, which may act either separately or simultaneously, viz.:—

(1) Dilution, the effect of which may be either to favour or to inhibit coagulation, according to the nature of the colloid.

(2) Change of temperature, which always assists coagulation.

(3) Addition of certain salts, the action of which is electrolytic; these must be selected so as to be of an electrical character opposite to that of the colloid which it is desired to coagulate.

Coagulation may also be accompanied—as, according to Weber, in the case of vulcanisation, though this is not admitted by Ostwald—by chemical combination, and often by dehydration. The latter occurs in the case of silica and iron hydroxide, and the reaction may be regarded, in a sense, as one of etherification.

Low temperatures may also bring about the coagulation of colloids. In this case the change of state is evidenced by the fact that when the temperature rises again above the congealing point colloidal substances are precipitated.

Sabanejew has made use of this property to effect a classification of colloids. He divides them into two great classes:—

(1) Lower colloids. which are *not* coagulated by freezing their *sols*, examples of which are albumin, dextrin, molybdic acid. The molecular weight of bodies of this class is below 3,000.

(2) Higher colloids, which *are* coagulated when their *sols* are frozen. This class includes rubber, starch, and the sulphides of copper and antimony, and their molecular weight is above 3,000.

The colloids of the first class lower the freezing point of water, whilst those of the second have no influence upon it.

For fuller details the reader is referred to Ostwald's excellent work on colloids.

To return to the coagulation of latex and the various theories propounded on that subject. Valuable and suggestive results were already obtained by Weber in his study of the coagulation of *Castilloa* latex.

The contention of Weber, whose earliest experiments were published in the *India Rubber Journal* in 1904, was that coagulability is not a specific property of the latex itself, but is dependent upon the presence of the coagulable proteins, the rubber-yielding substance being not dissolved in the serum, but emulsified in it.

"The coagulability is entirely dependent upon the presence of coagulable albuminoids, and, consequently, the treatment of rubber is strictly comparable, from the chemical point of view, with the clarification of wines or beer by means of albuminoids such as gelatin. It follows that the coagulation of a rubber latex can be effected by means of any of the precipitants of protein. If follows also that the rapidity of coagulation is a function of the nature of the albuminoids, and of the amount of inorganic material present in the serum. This is the reason why two latices of different botanical origin, although containing the same amount of protein, cannot be coagulated in the same way nor by the same methods. Some may be boiled without coagulation ; others coagulate before reaching the boiling point

"In presence of substances which interact vigorously with protein, such as the mineral acids, formic acid, acetic acid, tannin, hydroferrocyanic acid, mercuric chloride, etc., coagulation is instantaneous. The coagulum of necessity occludes the protein, and hence must be dried and rendered aseptic with the utmost care if fermentation is to be avoided."

The process of smoking, which provides at once a coagulant—acetic acid—and an antiseptic—creosote—realises these two conditions perfectly, and one would suppose that products prepared by this method should be almost perfect.

Nevertheless similar results can be achieved by other means. Weber suggests the addition to the filtered latex of formaldehyde, followed by dilution with a 10 per cent. solution of sodium sulphate. In this way one can obtain rubber almost free from protein[1] even in the case of latices containing large quantities, like *Castilloa.*

Instead of formaldehyde, formic acid, tannic acid, or acetic acid may be used ; the first of these acids is the best of coagulants, and is at the same time an antiseptic.

Other coagulants that may be mentioned are phosphotungstic acid, bismuth and potassium iodide, mercury and potassium iodide, chloral hydrate, and picric acid, but the high price of these compounds is against their employment.

As soon as it is coagulated the rubber must be thoroughly washed[2] in order to remove all soluble salts, then passed between rolls in order to convert it into the form of crêpe, which is dried at a low temperature in the dark.

The results which we have just described have been contested by Tromp de Haas and de Jong.[3]

To the presence of the film of protein enveloping the globules of the terpene antecedent of rubber, Weber attributes the possibility of coagulating latex by the addition of substances, like tannin, which precipitate protein.

By repeated washing, Tromp de Haas and de Jong prepared from *Castilloa* latex a cream containing all the globules, but entirely free from protein, which was shown by analysis to have been removed with the washing water. This cream cannot be coagulated by protein precipitants, but coagulates readily on heating. These chemists claim that Weber was wrong on two

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[1] It would appear from the results of more recent investigation that the production of a rubber free from protein is by no means desirable from the industrial point of view, since its presence influences in a remarkable manner, either directly or indirectly, the vulcanising capacity of the rubber. (See Beadle & Stevens, *Indiarubber J.*, 1912, 44, 554-555, 603-604 ; 1914, 47, 403-406)

[2] Eaton and Grantham's results (*Agric. Bull.*, Fed. Malay States. 1915, 4, 58-62) seem to indicate that a period of maturation should be allowed after coagulation and before the coagulum is mechanically treated.

[3] Teysmania, xv., Nos. 6–7.

points, one in affirming that the rubber from fresh latex is, like coagulated rubber, insoluble in ether; and the other in claiming that the film which envelopes the globule consists of protein.

They maintain that the rubber of fresh latex is taken into solution by ether, with which, when saturated, it forms a *gel*, and they state that the envelope of the globule is composed of a resinous substance, soluble in alcohol and acetone, which explains why these liquids bring about the coagulation of latex.

Harries, as the result of work on the fresh latex of *Ficus magnoloides* and *Ficus elastica*, seems to share their opinion, especially with regard to the solubility of rubber, in its nascent state, in ether; he holds, however, that the size of the molecule, if it could be measured accurately, would be found to be different for every rubber, the elementary composition remaining the same. Weber[1] replied to his critics that to him it was indisputable that the rubber was present in the latex in the form of a thick oil, enclosed in the protein film, and that, moreover, microscopical examination furnished an undeniable proof of this. As for the solubility in ether determined by his opponents and by Fendler, he attributed that to the use of alcoholic ether.

The discussion on this point could not be closed until Harries, later on, showed that freshly precipitated rubber is always soluble in ether, but that after extracting the resins by means of acetone, and drying, it becomes insoluble in that solvent, and is only rendered soluble again by boiling with acetic acid.

Esch and Chwolles,[2] on the basis of John Hart's practical observations, attempted to cut short the discussion. In their view, latex does contain rubber in the form of an oil which can be transformed into solid rubber, by the action of hydrochloric or acetic acid; Weber's view of this was correct. Where he went wrong, however, was in affirming the insolubility of rubber in ether, either in the nascent state or after coagulation, for Fendler,[3] like Esch and Chwolles, had obtained ethereal solutions as limpid as those in benzene; but this point is of secondary importance.

The interesting thing to know is whether the rubber is present in the latex in the solid state, or in the form of an oil. Harries definitely obtained an oil by evaporating ethereal solutions of nascent rubber; Weber's views on the nascent state of rubber have, therefore, been confirmed.

Ditmar[4] shared the view of Esch and Chwolles. In reality the discussion went further. The phenomenon of coagulation may be interpreted in two ways. Either it is due to a chemical reaction, that is *coagulation* properly so-called—before Victor Henri, Weber's interpretation explaining it by the precipitation of protein, appeared the most logical; it was an action similar to that brought about by gelatin in the clarifying of wines—or it is a physical effect, the globules scattered throughout the serum being brought together by mechanical means, such as centrifugal action, that is to say, *coalescence*.

The two methods can, moreover, be employed in conjunction in the case of a latex.

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[1] *Gummi Zeit*, 1903, 18; *Caoutchouc et Guttapercha*, 1903, 99.

[2] *Gummi Zeit.*, 1903, 18; *Caoutchouc et Guttapercha*, 1905, 2, 100.

[3] Fendler obtained ethereal solutions of Para Rubber of 97 per cent. strength.

[4] *Caoutchouc et Guttapercha*, 1905, 2, 102.

But there is the same difference between *coagulation* and *coalescence*, in Weber's language, as between butter and cheese, and in the formation of these masses polymerisation, about which we know nothing, or next to nothing, must play a very important part. It is probable that in *coalescence* the rubber does not polymerise as in *coagulation*, and that one has to deal with two different complexes.

Weber was very definite upon this point:—"Coagulated rubber," he said,[1] "has not the same properties as the product obtained by *coalescence*. That is the reason that the method of centrifuging, which has been tried in Ceylon, has not given good results; the products obtained in this way are not comparable with the products prepared by coagulation with acetic acid, and in the case of *Hevea* rubbers the difference between them is very sharp."

The same conclusions were arrived at by Flamant, in studying the latices of *Funtumia* and *Landolphia* and isolating the protein from them.

"Any substance which acts upon the whole of the protein and coagulates it will at the same time bring down with it the whole of the rubber; but if the action upon the protein is only of a partial character the precipitation of the rubber will be incomplete." [2]

From *Funtumia* Flamant isolated two proteins, only one of which is precipitated by acetic acid; precipitation of the rubber from *Funtumia* latex by acetic acid is, therefore, slow and quite incomplete.

The addition of pyrogallol, which precipitates these proteins slowly, results in the formation of a flocculent precipitate of rubber, lacking cohesion.

Flamant concluded: (1) that the coagulation of rubber is due to the proteins; (2) that by studying the character and reactions of the latter uniformity in coagulation can always be arrived at; (3) that the fewer proteins a latex contains the more readily coagulable it will be.

Gardner's Theory.—Gardner[3] neither supports the theories of Victor Henri nor shares Weber's views, but is of the opinion that electro-chemical coagulation is a purely physical phenomenon.

The globules are distributed throughout the serum at intervals which vary according to the type of latex and to its character. At the moment of tapping they are mixed, but, on standing, the largest rise first to the surface. Since rubber is lighter than water, or than the serum, it follows that if a more or less stable state of equilibrium does not exist, the rubber should rise at once to the surface of the latex. In this case such rising is hindered by the Brownian movement. As the rubber is in an emulsified state, its coagulation must be preceded by de-emulsification, or by a disturbance of the physical equilibrium of the liquid.

An emulsion being the result of surface tension phenomena, and its various constituents being of different densities, the rubber globules should rise slowly to the surface, and there agglutinate.

Coagulation, as Spence also holds, is independent of proteins.

In support of this theory, Gardner quotes the following experiment:—

"Coagulable proteins, such as those found in latex, do not diffuse through a membrane, but if they be converted into non-coagulable

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[1] *Le Caoutchouc et la Guttapercha*, 1912, 9, 5940.
[2] *Le Caoutchouc et la Guttapercha*, 1912, 9, 6135.
[3] *Le Caoutchouc et la Guttapercha*, 1905, 2, 351.

albuminoids, by digestion with papaïn at 50° C. for 36 hours, they will diffuse; this can be shown by means of the xantho-proteic reaction in the diffusate.

"By this means, then, it is possible to free the rubber latex from protein, and if now this purified latex be poured into absolute alcohol ($d = 0{\cdot}794$), it is at once precipitated as a fine powder, which can be collected, and, by kneading, converted into a tenacious substance."

According to Gardner, this shows that the proteins have nothing whatever to do with coagulation, and that the membrane enveloping the globules is composed of some other substance. This membrane, moreover, resists the action of papaïn.

The proteins probably function as emulsifying agents, but play no part in the process of de-emulsification.

The permanence of the physical equilibrium in the latex is dependent on the viscosity of the emulsifying agent, in the case of the albuminoids, and also on the size of the globules; the smaller the latter, the greater will be the viscosity of the latex.

De-emulsification depends chiefly upon the production of a negative surface tension by disintegration of the membrane, continuous or discontinuous, surrounding each globule of rubber.

Alcohol greatly reduces the surface tension of the mother-liquor, and, when present in sufficient quantity, reverses its sign. Thus the coagulation which it brings about is due purely to a physical cause.

Coagulation by acids is less easy to explain. The hypothesis put forward by Gardner is as follows:—The resins are present in the latex in the form of unstable compounds, and, if particles of these resins constitute the membranes round the rubber globules, de-emulsification may be explained by the chemical decomposition of these unstable compounds by the acids, and the resultant establishment of a negative surface tension.

Gardner concludes from these experiments that coagulation of latex is a purely physical phenomenon.

This question of coagulation, which is of great scientific interest, is of still greater interest from the technical point of view, for upon the character of the coagulum obtained depend the mechanical qualities of the rubber and its lasting properties. Thus the problem is really a very serious one, and it will be seen that, in spite of the labours of many workers, it has remained for a long time in a very obscure condition. Victor Henri's work has contributed a more likely solution, and in all probability indicates the true principles underlying the coagulation of latex. The chief results of this work may now be briefly summarised:—

Victor Henri first investigated the electrolytic conductivity of latex, and found in the case of a *Hevea* latex, the value $3{\cdot}3 \times 10^{-6}$, a figure which corresponds with that of a 0·25 per cent. solution of sodium chloride.

He then noticed that the Brownian movement of the globules is completely arrested by adding a 20 per cent. solution of sodium chloride to the latex, and he states that this addition does not bring about coagulation. This assertion is open to discussion, and could not be held to be true generally, for sodium chloride in the form of sea salt is actually used as a coagulant in some districts, and in concentrations much lower than those employed by Henri.

The depression of freezing point, which gives an indication in round numbers of the molecular concentration of the substances dissolved in the latex, amounts to $\Delta = 0{\cdot}22°$ C. This corresponds approximately to an $\frac{N}{6}$ solution of a non-electrolyte, or to an $\frac{N}{16}$ solution of an electrolyte.[1]

These facts, which Henri was the first to observe, are of great interest, for the nature and the concentration of the salts present are of cardinal importance from the point of view of coagulation.

It had been laid down as a principle, and that is Weber's theory, that the proteins play the principal part in the coagulation of latex. Victor Henri adopted an entirely different standpoint, and this is what gives to his work its very great interest, and its absolutely novel character.

His first experiments were, he tells us, directed towards the determination of the effect products by the addition of different substances to latex, which had been purified by dialysis. It was found that all latices thus purified are coagulated by certain liquids, such as various alcohols.

Latex may be regarded as a suspension of very small particles in an aqueous liquid, more or less rich in (inorganic) saline or organic compounds; on coagulation the globules unite to form a clot. It is, therefore, natural to enquire what are the general properties of such fine suspensions; to ascertain whether there are not other suspensions in which this agglomeration of the particles might be investigated, and lastly to try and find out what are the essential conditions of this agglomeration. These suspensions or emulsions are similar, as already indicated, to colloidal solutions; the same general laws should, therefore, govern the precipitation of colloids and the agglomeration of the particles of fine suspensions.

It is known that the precipitation of colloids is brought about, more particularly, by electrolytes, and that precipitation is largely influenced by the nature of the salts, acids, and bases present; so that if it be desired to study the precipitation of a colloid systematically, it is necessary to work with solutions as pure as possible.

In the case of rubber latex the same technique must be adopted, and the whole of the dissolved substances removed from the serum to begin with. It may be remarked that a somewhat similar process was employed by Tromp de Haas in his experiments. To bring about this purification, Victor Henri dialysed latex in collodion bags, changing the external water daily. In this way a latex is obtained which contains no appreciable quantity of salts, as shown by the reduction of its electrolytic conductivity to the neighbourhood of that of distilled water, and by the fact that the depression of freezing point is less than 0·01° C.

In considering the addition of various substances to the latex, three cases present themselves:—

(1) Where no effect is produced, the liquid remaining white and milky, without flakes.

(2) Flakes are formed, but remain isolated, either rising to the surface or sinking to the bottom, not, however, uniting with one another. These flakes are sometimes very small like the particles of a pulverulent precipitate; sometimes they are as large as 2 or 3 mm. in diameter. Agitation does not tend to unite them, but only to break them up into still smaller flakes. This phenomenon is identical in character with that of the *agglutination* of the red blood-corpuscles, or of the fat globules in milk. Henri speaks of

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[1] *Le Caoutchouc et la Guttapercha*, 1906, 3, 511.

it as *agglutination*, and it is a phenomenon very similar to the *coalescence* of Weber. It is characterised by the fact that on the addition of water, or on agitating the liquid, the aggregates of flakes break up; in other words, the phenomenon is a *reversible* process.

(3) A network of very long filaments is formed, uniting the whole of the globules in the latex; this network is elastic; if the latex be shaken, the filaments unite with one another, and a clot is obtained, the structure of which becomes more and more close-knit, and which cannot again be separated into fragments by shaking. This phenomenon is *coagulation*, and the change which occurs is *non-reversible*—that is to say, the coagulated globules are no longer separable by addition of water or by agitation.

Victor Henri's Experiments.—Victor Henri studied consecutively the action of single substances and of mixtures on latex. The conclusions arrived at by him are as follows:—Ethyl, methyl, or amyl alcohol alone have absolutely no effect upon dialysed latex in whatever proportion they may be added. This result somewhat upsets the accepted ideas on the subject, and shows that coagulation by alcohol is dependent on the presence of dissolved salts in the serum.

The salts of the monad metals, sodium and potassium, and of ammonium have no effect, whatever quantity be added.

The salts of calcium, magnesium, and barium cause *agglutination* in the dialysed latex, when added in sufficient quantity; the concentration of the salt must exceed that of a normal solution.

The salts of the heavy metals, Mn, Fe, Ni, Co, Cu, Zn, Pb, Al, produce *agglutination* in concentrations lower than those necessary in the case of the alkaline-earth metals; an $\frac{N}{20}$ solution is sufficient, and the effect is independent of the nature of the acid radicle. Up to a certain limit of concentration very small flakes are formed; as the concentration increases above this limit the flakes become larger, but an elastic clot is never obtained.

Alkalis have no effect.

Acids produce *agglutination* at concentrations in the neighbourhood of $\frac{N}{2}$, and hydrochloric, nitric, and acetic acids have equal effects; sulphuric acid is active at lower concentrations. As the concentration is increased *coagulation* begins to take place.

Trichloracetic acid occupies a place by itself; even at very low concentrations it produces *coagulation*, an elastic clot being formed. This acid is one of the characteristic reagents for protein, and its very distinctive action would, therefore, lead one to suppose that there is a good deal of truth in Weber's theory of the protein envelope round the globules. Acetone also coagulates dialysed latex.

Henri now extended his work to the investigation of the combined action of alcohol and various electrolytes. In practice the alcohol in such mixtures may be replaced by another substance.

Speaking generally, when any salt or acid is added to a dialysed latex, in sufficient quantity, and alcohol is afterwards added, either *agglutination* or *coagulation* is brought about.

From this standpoint a sharp distinction is to be drawn between the salts of the monad metals and the divalent and trivalent acids and salts. In presence of the salts of the monads, K, Na, NH_4, alcohol only causes *agglutination*, and in order for this to occur the salts must be present in fairly high concentration, about 100 to 200 grammes per litre. In the presence of the salts of divalent metals, even in such small concentrations as $\frac{N}{100}$, the addition of alcohol causes coagulation, a very elastic clot being formed.

By gradually reducing the amount of alcohol added, whilst keeping the salt concentration constant, it can be shown that small quantities of alcohol only produce agglutination, whilst still smaller quantities have no effect at all.

A similar gradual passage from *coagulation* to *agglutination* may be observed when the quantity of alcohol added is kept constant, whilst the salt concentration is gradually reduced.

Coagulation may, therefore, be regarded as an extreme case of *coalescence* or *agglutination*, since one and the same reagent is able to bring about the one or the other, according as it is added in smaller or greater amount. Acids act, in conjunction with alcohol, like salts; alkalis are without action.

The latter fact, which is in line with similar observations made in the case of colloids and of other emulsions, leads necessarily to the investigation of the influence exerted by the reaction of the liquid upon the coagulation and agglutination of latex.

On adding a metallic salt, or an alcohol, to dialysed latex which has been made alkaline with soda or potash, it is found that an extremely small quantity of alkali is sufficient to alter entirely the course of the change which occurs. Thus the addition of 1 part in 10,000 of normal soda is sufficient to inhibit *agglutination*, or to determine the occurrence of the latter instead of coagulation. For example, on adding to dialysed latex magnesium chloride, followed by alcohol, a clot is formed; but if the latex be first of all rendered very faintly alkaline, isolated flakes only will be formed on the addition of these reagents. The effect produced by alkali shows that the passage from *agglutination* to *coagulation* is gradual, and that *coagulation* may be regarded as a limiting case of *agglutination*.

It may be asked, of what interest is it to establish this fact?

In the case of colloids only cases of precipitation and of *agglutination* have been taken into consideration; the laws governing the precipitation of colloids apply well to the phenomenon of agglutination, but it was not known whether *coagulation* might not be something quite different in character, a special phenomenon to which the laws discovered in the investigation of the precipitation of colloids would not apply.

It was, therefore, necessary to know the relation between *agglutination* and *coagulation*. Since then the latter has been shown to be a limiting case of the former, all the laws found to govern the precipitation of colloids are applicable to *coagulation*.

Under these circumstances it became of value to know something about the nature of the electric charge on the globules.

It is, in fact, known that any emulsion or colloidal solution is formed of particles which are electrically charged with reference to the medium in which they are suspended.

Thus, a fine suspension of china clay in water contains particles which are charged negatively with respect to the water; and, in the same way, colloidal ferric hydroxide is composed of ultramicroscopic particles which are positively charged. In order to determine its "electrical sign" the emulsion is introduced into a **U**-tube with platinum electrodes, and a difference of potential of 110 volts is applied. In a few moments migration of the particles begins, the liquid becomes clear at one of the electrodes and the particles of the emulsion accumulate round the other.

When latex is treated in this way it rapidly becomes clear round the negative electrode; consequently the globules are *negatively* charged with respect to the liquid in which they are suspended.

It is essential to know the nature of the electric charge of an emulsion, because by it precipitation is governed.

It is, in fact, known that the precipitation of *negative* emulsions is brought about by acids, and by the salts of di- and trivalent metals, irrespective of the nature of the acid radicle.

On the other hand, *positive* emulsions are precipitated by *alkalis*, and salts of di- and tri-basic acids, irrespective of the particular metal present.

These laws are applicable to latex, and afford a clear explanation of why the salts of monovalent metals behave differently towards it from the salts of di- and trivalent metals; it is easy to see also why acids have an action and *alkalis* have none.

Victor Henri's work is thus of the highest importance, since it has revealed the mechanism of coagulation, and thrown light upon a process which was quite empirical. It is true that investigations were limited to *Hevea* latex, but it is a simple matter to carry out the same determinations with other latices, and so to effect a judicious choice of coagulants, designed to yield the best possible rubber.

The industrial value of the rubbers obtained will, therefore, vary within very wide limits, according to the nature and proportion of the reagents employed, and in the following table are shown the results of mechanical tests made by Henri on vulcanised samples prepared from rubbers coagulated in different ways:—

VICTOR HENRI'S TABLE.

	Methods of Coagulation.	Breaking Strain. (Grm. per sq. mm.)	Elongation at Break. (= No. of times Original Length.)
1	Heating and evaporation at 80° C., . . .	170	6·2
2	,, ,, 25° C., . . .	190	5·0
3	Dilute acetic acid, ...	175	7·5
4	Concentrated acetic acid, ...	210	7·1
5	Trichloracetic acid, ...	325	6·0
6	,, ,, + electrolyte, . . .	310	5·3
7	Mixture 6, washed, ...	380	5·2
8	Dilute trichloracetic acid + two saline coagulants,	490	5·6
9	Strong ,, ,, ,, other ,,	660	6·2
10	Commercial cut-sheet, ...	180	4·3

From this brief synopsis it will be realised what an important part is played by the coagulant in determining strength and elasticity.

Victor Henri's work on this subject was rounded off by an investigation into the structure of the clot of rubber formed on coagulation, a subject of equal interest.

The investigation was carried out by two methods, the macroscopic and the microscopic. If, when coagulating latex, sufficient care be taken to avoid the least disturbance of the latex, it will be observed that the structure of the clot is always the same, for the same coagulant. In some cases the rubber collects at the bottom of the vessel in which the process is being carried out, in the form of small flakes, more or less isolated from one another, or perhaps in masses which remain disunited.

In other cases all these separate particles or masses unite together and form a tenacious network; this network is elastic, and if the clot be raised by one end it is possible to lift it bodily from the liquid. *The structure of the clot varies with the coagulant used.* Sometimes the mesh is very open, and in this case the elasticity is small; sometimes it is very close, and the clot is then highly elastic. An examination of the connection between the coagulants and the various forms of coagulum shows that:—

(1) Weak coagulants, or *agglutinants*, give isolated flakes, or a clot with open mesh.

(2) Powerful coagulants give close-meshed coagula.

Speaking generally, it may be said that the chief factor determining structure is the reaction of the liquid.

In presence of alkali, isolated flakes, or open-meshed networks are always formed. In neutral liquids, di- or trivalent salts produce close-meshed networks. In presence of acid, either when acids alone are used or, better, a mixture of acid and di- or trivalent salts, or alcohol, or acetone, a clot with a very close and very elastic network is produced.

It follows that with one and the same latex it is possible to obtain coagula which are structurally quite dissimilar by using different coagulants, and varying the acidity of the liquid. Moreover, this structural difference persists when the coagulum is dried; a clot with a very close mesh always gives a strong, elastic rubber, whereas a clot with an open network gives a rubber which is weak and "short." A question here suggests itself—viz., as to whether the defective coagulation produced by a reagent which, for example, gives only isolated flakes, cannot be afterwards corrected by the addition of other coagulants which yield an elastic clot. This question is of great technical importance.

By precipitating a latex with a mixture of soda and calcium chloride Henri obtained isolated flakes, but he noticed that, on acidifying the mixture, these flakes united together to form a close elastic network.

It follows that a faulty coagulation can be corrected by the addition, to either the fresh or the dried latex, of acid or other appropriate coagulant.

Microscopic Observation of the Process.—The process of coagulation may also be studied by adding various coagulants to the latex under the microscope. The manipulation is not quite simple, for at the moment when the coagulants are added a general movement of the latex occurs which makes observation difficult. It is, therefore, necessary to resort to various artifices in order to slow down this movement, and when this is done a series of valuable observations can be made.

When coagulation is produced by means of an alkaline reagent, such as a mixture of soda and calcium chloride, the globules which are at first in continuous motion, join up into irregular groups of 20 to 50, and then form still more bulky masses. It is noteworthy that these masses are always irregular in form and exhibit no kind of structure in the field of the microscope; on the contrary, a simple displacement of the cover glass is sufficient to alter their shape and to break them up; there is no cohesion between the particles of which they are composed.

On coagulating with an acid reagent the behaviour of the globules is different. At first a few globules unite to form a kind of nucleus; then numbers of chains are formed by the union, in straight lines, of globules, the Brownian movement of which becomes reduced, if not entirely arrested. These chains of globules move in different directions across the field of the microscope. Sometimes fresh globules come and unite laterally with one of the chains, anastomosing with it, as it were. The final result of the crossing and recrossing of these chains is the formation of a network, and thus microscopic analysis gives, broadly, results which are absolutely identical with those obtained macroscopically.

According to the coagulant used, either agglutination, or coalescence, or coagulation takes place, and either precipitates or networks are produced. The fineness of the network is a true index of the elasticity of the clot.

Optical examination thus confirms, once more, the conclusion that all our knowledge of colloids, *sols*, and *gels* is applicable to rubber.

The alignment of the globules, their forming up into absolutely straight lines under the influence of acids or electro-positive coagulants, is in agreement with Bütschli's observations on oil emulsified in gelatin or albumin, and with Cotton and Mouton's work on colloidal iron hydroxide. It follows that the form and structure of the rubber coagulum, and as a consequence its physical properties, elasticity, nerve, strength, are absolutely dependent upon the conditions under which coagulation takes place.

The same is true of coagulation or precipitation of cellulose and of nitrocellulose. It should be possible, with the aid of these very clear conclusions of Victor Henri's, to deduce from the physico-chemical characteristics of a latex, a series of reasoned methods of coagulation, varying with the species, which would enable us, by properly selecting the coagulant to produce a rubber with constant technical properties. Unfortunately these ideas, as accurate as they are new, have not become widely disseminated, and people prefer to have recourse to empirical methods which in many cases have little to be said for them. In Harries' language, " In rubber circles the intrusion of science is viewed askance, and all possible steps are taken in many cases to keep it out."

Spence's researches on *Funtumia elastica*[1] confirm Victor Henri's results.

From the point of view of the dialysis of latex with reference to electrolytes, Spence finds that negative ions prevent agglutination, whilst positive ions assist it. His conclusions with regard to alkalies, salts, and acids are the same.

He finds, however, that salts of iron act more energetically than those of the alkaline-earth metals. If ammonium sulphate be added to a latex until the latter is saturated with regard to that salt, and if then a quantity of the double chloride of calcium and iron be added, the globules separate from the serum and rise to the surface, leaving, according to Spence, a clear liquid beneath them. The cream thus formed may be readily transformed into crude rubber, by adding to it a mixture of equal parts of acetic acid and an alcoholic solution of creosote at 20° C.[2]

The rubber obtained by the use of the centrifugal separator is imperfectly coagulated. Spence endeavoured to provoke coagulation by digesting the

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[1] *Le Caoutchouc et la Guttapercha*, 1908, 5, 1632.

[2] Vienna Lecture, 1910.

nitrogenous substances present in the latex, by means of trypsin or pepsin, but obtained only negative results.

Spence favours the theory of Victor Henri, and does not uphold Weber's views relative to protein enveloping membranes; his view is that the substances in suspension in the latex are in a state of equilibrium in virtue of the negative charge or of the surface tension of the particles. Coagulation is only the result of a disturbance of this equilibrium.

Moreover, the whole of the nitrogen found in the latex is not there in the form of protein; dialysis reveals the presence of crystallisable nitrogenous compounds, as shown by Spence.

After our explanation of Victor Henri's theory no benefit is to be derived from going into details as to the various substances employed in order to bring about the separation, by chemical means, of rubber from serum. All are good if used in the right way, and so as to fulfil the conditions indicated by Henri. We may, however, refer to the special position which he has assigned to trichloracetic acid. Nevertheless, since the latex contains ferments, it is obvious that given equality in coagulating value, the preference will be given to that reagent which is at the same time an antiseptic; or, in selecting reagents to form a coagulating mixture, one of them will always have to be an antiseptic. This method is adopted in Ceylon and in the Dutch E. Indies, where the coagulating mixture contains acids, such as acetic or trichloracetic, and formaldehyde, mercuric chloride, or alum.

Vernet,[1] who has seen these processes in operation, has found that with their aid it is possible to obtain quite superior rubbers even from low-grade latex.

It now remains to consider briefly those methods of coagulation which do not involve the intervention of physico-chemical action in the formation of the clot.

Smoke Coagulation.—The most important of these is the process of smoking, which is made use of in the preparation of the most highly valued rubber, Para.

According to Vernet[2] coagulation is due in this case to the simultaneous action of several factors.

(1) The heat from the fire used.

(2) The creamy condition of the latex, which has become acid as the result of incipient fermentation.

(3) The products of distillation of the wood and the oils contained in the smoke—that is to say, carbon dioxide, acetic acid, formic acid, and creosote.

The processes going on side by side are, then, coagulation by the rapid evaporation of the serum as it is exposed in a thin layer to the action of heat; coagulation by the organic acids, acetic and formic, formed by the pyrogenic decomposition of the vegetable fuel; coagulation by the acids formed by incipient fermentation of the serum; and antisepsis by the creosote contained in the smoke.

The choice of fuel for the production of the smoke must play a large part in determining the success of the operation, and one can understand why, outside Brazil, this process, which demands considerable skill to carry out, has never given any but imperfect results. On the Amazon, in addition to resinous or green woods, more particularly that of the *Itanba*, the *seringueiro* uses as fuel oleaginous fruits such as those of *Attalea excelsa* (*Urucuri*),

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[1] *Le Caoutchouc et la Guttapercha.*

[2] *Le Caoutchouc et la Guttapercha,* 1912, 9.

Maximiliana regia (*Inaja*), *Maximiliana princeps* (*Motacu*), *Manicaria saxifera* (*Rocouri*), and *Bertholettia excelsa* (*Almendras*).

According to several chemists who have been able to investigate, on the spot, the composition of the smoke of the *buyons*, the principal constituents are nitrogen, carbon dioxide, carbon monoxide, acetic acid, formaldehyde, creosote, phenol, tar, and water vapour; and Nors[1] claims that the smoking process confers on rubber the quality of resistance to an extent not possessed by an acid-coagulated rubber.

Other Methods.—Centrifugal separation was employed a good deal, as we have seen, in the early days of plantation rubber. This process permits of the separation of the suspended globules, in the form of a thick cream, but does not bring about true coagulation, to obtain which chemical reagents must be added, or the latex must be heated.

Similar objections apply to the process of separation by dilution of the latex with water, and thus increasing the density of the serum. The Brownian movement renders this process a slow one, and it is always necessary to finish it off by desiccation.

Coagulation by fermentation is a process sometimes employed in Africa. As this process is carried out in the presence of urine,[2] it is probably due to the influence of special diastases; no alcohol is formed, and the mass remains neutral, although developing an unbearable odour of butyric acid.

Eduardoff[3] and Weys[4] describe a method of coagulation by catalysis, in the cases respectively of *liana* latex, and latex of *Ficus elastica*. The method consists in adding to the latex a fragment of recently prepared rubber, and appears to be quite analogous with the inoculation or seeding of a saturated solution with a crystal of the dissolved salt. By applying Victor Henri's results coagulation might also be brought about electrolytically, the globules migrating to the cathode under the influence of the current, but no experiments on a practical scale would appear to have been made in this direction.

In the following tables the results of analyses of a number of different samples of rubber are given. The samples were obtained by different methods of coagulation, and for the sake of comparison the figures for smoke-cured Amazon rubber are also given:—

WASHED RUBBER FROM *HEVEA BRAZILIENSIS.*

	Ceylon Biscuits. (Bamber.)	Ceylon Lace. (Burgess.)	Ceylon Worms. (Ballantyne.)	Pale Crêpe. Malay States. (Ballantyne.)	Dark Crêpe. Malay States. (Ballantyne.)
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Caoutchouc, . . .	94·60	94·08	91·55	93·27	93·60
Resins (acetone extract),	2·66	2·68	3·50	3·60	3·02
Oxygen, . . .	...	...	...	...	...
Protein, ...	1·75	2·62	3·85	2·36	2·56
Mineral matter, . .	0·14	0·12	0·20	0·27	0·30

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[1] In Ceylon and the East Indies the smoking process is very frequently used with rubber which has been prepared by coagulation with acid. M. Ridley has been the promoter of this method of treatment, which gives results comparable with fine hard Para. A number of constructional engineering firms now undertake the installation of complete smoking plants.

[2] Doppart, *Le Caoutchouc et la Guttapercha.*

[3] *Gummi Zeit*, 1909, 23, 809.

[4] *Poefstatin of Java*, 1910.

All the above rubbers were coagulated with acetic acid, dried *in vacuo*, and washed until their reaction was neutral.

The following are figures for smoke-cured Para (washed) :—

SMOKE-CURED PARA (WASHED).

	Fine Para. Upper Amazon. (Michelin.)	Fine Para. Brazil. (Esch.)	Extra Fine Para. Brazil. (Esch.)
	Per cent.	Per cent.	Per cent.
Caoutchouc, ...	98·87	91·90	90·30
Resins (acetone extract), . .	2·62	1·90	2·00
Oxygen, ...	...	2·20	2·30
Protein, ...	...	2·90	4·10
Moisture, ...	0·32	...	...
Ash, ...	0·29	1·10	1·30

WASHED RUBBER FROM *HEVEA BRAZILIENSIS* (TONKIN).

Michelin.

	Smoked Rubber.	Rubber fermented under alkaline conditions.	Rubber coagulated naturally.
	Per cent.	Per cent.	Per cent.
Caoutchouc, ...	94·60	97·32	97·02
Resins (acetone extract), . .	4·00	2·18	2·44
Moisture, ...	0·68	0·30	0·15
Ash, ...	0·62	0·30	0·39

WASHED RUBBER FROM *HEVEA BRAZILIENSIS* (TONKIN).

Michelin.

	Rubber coagulated with Acetic Acid.	Rubber coagulated with Acetic Acid and Formaldehyde.	Bark Scrap.	Lumps.
	Per cent.	Per cent.	Per cent.	Per cent.
Caoutchouc, ...	95·87	95·14	94·34	95·78
Resins (acetone extract), .	3·59	4·06	1·90	2·60
Moisture, ...	0·18	0·36	1·66	0·42
Ash, ...	0·36	0·44	2·10	1·20

"Cup" scrap contains only 94·68 per cent. of caoutchouc and 2·06 per cent. of resins.

It is worthy of note that the rubber coagulated with acetic acid and formaldehyde is the richest in resins.

WASHED RUBBER FROM *HEVEA BRAZILIENSIS* (TONKIN).

Bergougnan.

	Rubber coagulated by Fermentation.	Formaldehyde and Alum.	Acetic Acid and Formaldehyde.	Trichloracetic Acid and Formaldehyde.	Formaldehyde, Alum, and Trichloracetic Acid.	Lemon Juice and Formaldehyde.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Caoutchouc, .	95·90	99·30	99·30	98·15	99·30	99·30
Ash, . .	0·40	0·86	0·42	0·33	0·71	0·38
Resins, .	3·70	1·68	1·54	1·30	1·60	1·50

WASHED RUBBER FROM *HEVEA BRAZILIENSIS* (TONKIN).

Bergougnan.

	10 PER CENT. ACETIC ACID PER LITRE OF LATEX.				Formaldehyde 5 c.c., and 10 per cent. Acetic Acid 60 c.c. per litre of Latex.
	30 c.c.	60 c.c.	90 c.c.	120 c.c.	
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Caoutchouc, . .	95·20	95·80	97·60	97·90	95·60
Ash, ...	0·46	0·54	0·50	0·54	0·44
Resins, . . .	4·52	4·40	4·30	4·08	4·18

From the above figures it would appear that the best results are to be obtained with from 1 to 2 per cent. of pure acetic acid calculated on the volume of latex treated.

Of the mixed coagulants, the best results are obtained with formaldehyde and alum, acetic acid and formaldehyde, trichloracetic acid and formaldehyde; these produce very similar results.

Reintgen details the various methods of coagulation now in actual use in the different rubber districts, and the following is a summary:—

METHODS OF COAGULATION.

A. Coagulation by Heat—(1) *Natural Heat.*—(*a*) Drying on the tree, or on the ground—Ceara, Equateur, Central and Southern Africa, Madagascar. (*b*) Drying on the body—Congo, Angola, Zambesia, German East Africa.

(2) *Artificial Heat.*—(*a*) Dry heat and smoking—Amani, Ceara, New Caledonia. (*b*) Moist heat, or heating the latex—Mexico, Lagos, Congo, Tanga.

B. Coagulation by Addition of Water—(1) *Sea Water* (and fermentation). —Assam, Central Indies, French Congo, New Caledonia.

(2) *Hot Water* (and mechanical agitation).—Cochin China, Central Indies, Congo.

C. Coagulation by Chemical Reagents—(1) *Sea Water, or Salt Solutions.*—Eastern and Southern Brazil, Mexico, Senegambia, Sierra Leone, Madagascar, Malaysia, Borneo.

(2) *Salts, Acids, Vegetable Juices.*—Congo, Madagascar, Gambia, Cassamance, Bissao, Sierra Leone, Togo, Central America, Colombia, West Equateur, Western Peru, Ceylon, British and Dutch East Indies, Tonkin.

CHAPTER VIII.

EXAMINATION OF THE PHYSICAL PROPERTIES OF COAGULATED RUBBER.

RUBBER, when freshly coagulated, is by no means a pure product, but is contaminated and rendered impure by the presence of a number of substances, either derived direct from the latex, or formed as the result of bye-reactions—oxidation, fermentation—occurring during the formation of the rubber.

The purpose of raw rubber analysis is to determine the content of pure caoutchouc, in any sample, and to isolate and characterise these various impurities.

Up to the year 1883 no chemist had yet undertaken the task of devising a method of analysis of rubber, and the results of work done on this colloid, from that of Hérissant and Macquer, to that of Adriani and Bouchardat, both as regards its physical constants and its chemical properties, were scattered through a mass of literature.

At about this time, however, Heinzerling, in his book, *Die Fabrikation der Kautschuk und Guttapercha Waren*, collected together, for the first time, these scattered results into one body of doctrine, and attempted to establish a method of analysis.

This work was of necessity incomplete, for, quite apart from all that concerns vulcanised and manufactured rubber which does not come within the scope of this work, we find that Heinzerling left out of account certain extremely important points, and that, in particular, he entirely omitted to refer to the estimation of the oxidised rubber which is always present in natural rubber. Nevertheless, in spite of its omissions, up to the appearance of Chapel's work in 1892, and more especially the remarkable book by Seeligmann, Lamy Torrilhon, and Falconnet, *Le Caoutchouc et la Guttapercha*, in 1896, Heinzerling's treatise remained the only work which an analyst could usefully consult, supplementing what he there found with the work published during this period by Clarke, Classens, Cloez and Aimé Girard, Donath, Fabroni, Ure, Neer d'Eisen, and above all Dr. Robert Henriques.

The account of the physical and chemical properties of natural rubber, the examination of its internal structure, the study of its density, its permeability by water and alcohol, its dialysing and polarising power, its compressibility, its distensibility, its resilience, its adhesiveness, were set forth in an excellent manner by Seeligmann, Lamy Torrilhon, and Falconnet,[1] who knew how to display, with great lucidity, the whole of the knowledge on this subject which existed at the time their book was published. The same quality characterises their *résumé* of the analytical methods then known.[2] For all these elementary details, therefore, the reader may be referred to their excellent treatise.

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[1] *Le Caoutchouc et la Guttapercha*, 99–119.

[2] *Le Caoutchouc et la Guttapercha*, 223–227.

Nevertheless, as regards the physical properties, it is necessary at this point to give some details of the more recent investigations which have been carried out on the elasticity, the tensile strength, the effect of low temperatures, and the viscosity of solutions of rubber, and to summarise, as concisely as possible, the results of the extremely interesting work on the physico-chemical side carried out by Chauveau, Bouasse, Breuil, Boutaric, Axelrod, Terry, Schidrowitz, Victor Henri, and Frank. This branch of rubber research being essentially French, the special stress now laid upon it will be excused.

The density of crude rubber varies a good deal with the species, the method of coagulation, and the degree of purity of the rubber.

On the average it varies from 0·920 to 0·942 at 14° C.

Chapel and Bouquillon give the following values for the density at 16° C. of certain washed commercial sorts :—

Sort.	Density.	Sort.	Density.
Para, ...	0·914	Sierra Leone, . .	0·923
Peruvian, . . .	0·915	Senegal, . . .	0·929
Colombian, . .	0·915	West Indian Scraps, .	0·935
Madagascar, . .	0·915	Mozambique, . .	0·939
Sernamby, . . .	0·918	Ceara, . . .	0·958
Borneo—Prime, . .	0·916	Assam, . . .	0·967
Negroheads, . .	0·920		

The density of low-grade African sorts is generally higher, in some cases practically reaching unity. This difference in density is due, more particularly to the presence of resins which cannot be removed by crushing and washing with water, and the density of which is much higher than that of caoutchouc. Guayule also has a very high density—viz., about 0·970, which must likewise be due to the presence of impurities.

Para purified by the method of Harries has a density of 0·910.

In the course of an investigation in biological mechanics Chauveau[1] was led to examine the phenomena of the expansion and compression of rubbers, and succeeded in formulating the following principles, which have served either as bases for later work, or as valuable guides for technical purposes :—

The calling into play of the elasticity of rubber, by the addition or removal of a certain load, gives rise to two kinds of internal work in each case—viz., a displacement of the molecules in relation to each other, and a change in the dimensions of the intermolecular spaces.

The displacement of the molecules removes them from their equilibrium position, or restores them to it; in the former case external work is done on the rubber, and heat is produced thereby, whereas in the latter case external work is done by the rubber, resulting in cooling. Changes in the dimensions of the intermolecular spaces produce cold in the rubber if the dimensions become greater, and heat if they become less.

When the elasticity of rubber is called into play by compression, the displacement of the molecules is accompanied by contraction of the intermolecular spaces; both these kinds of internal work act in the same sense

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[1] *Comptes rendus*, 1899.

from a thermal point of view, both liberating heat. At the moment of decompression, both the restoration of the molecules to their equilibrium position, and the expansion of the intermolecular spaces result in the absorption of heat.

If the elasticity be brought into play by tension, the internal work which displaces the molecules from their equilibrium position is transformed into heat, but since at the same time the interspaces between the molecules are enlarged, cold is produced. When the tensile force is removed the inverse phenomena occur, there being simultaneous absorption of heat as the result of the molecules of the elastic body being restored to their equilibrium position, and liberation of heat resulting from the contraction of the intermolecular spaces.

The two kinds of internal work, then, resulting from elongation or contraction, act against one another from the thermal point of view, the one causing the liberation, the other the absorption of heat. The heat phenomena are strictly in conformity with the mechanical processes involved, and not only the sign (+ or —), but also the relative magnitude of the heat effect can be predicted from a consideration of the conditions controlling the two kinds of internal work. The displacement of the molecules is a function of the external work which is equivalent to the product of the force acting and the distance through which it acts. The change in the dimensions of the intermolecular spaces is a function simply of the distance through which motion occurs, if it be assumed that the change of volume undergone by a body when its elasticity is brought into play is proportional to the change of shape.

When compression takes place the two thermodynamic values referred to above are of the same sign, and are simply added together. Hence the simple heating and cooling which take place on compression and decompression respectively, both represent, very accurately, the arithmetic sum of these two values.

Under tension the two values to be added are of opposite sign, and consequently the total heat effect on elongation or contraction of an elastic thread always represents the algebraic sum of the two opposite effects. Since the variations in these two effects do not follow a parallel course, one being proportional to the product of the force applied and the path, whilst the other is proportional to the path only, there may occur numerical equality between them at a certain point during the increase or decrease of elongation or contraction. At this point, therefore, the resultant heat effect will be nil, and the point will be a point of inflection. Knowing the conditions of the two kinds of internal work, this point of equality may be regarded as inevitable, as also the thermal neutrality resulting from it, both in the case of elongation and in that of contraction.

But the thermal inflection is necessarily of opposite sign in the two cases: it is logical to suppose that the point is the more rapidly reached the greater the extensibility of the elastic body. Thus, in the case of the negative work produced by the elongation of rubber, the neutral point of inflection is preceded by a brief phase of cooling, followed by the principal phase of rise of temperature.

In the same way when positive work results from the contraction of rubber, the neutral point of inflection is preceded by a brief heating phase, and followed by the principal phase—viz., absorption of heat.

These experiments, both on extension and compression, may be carried out by adding or taking away a load either in one operation, or in a number of stages, consisting of equal fractions of the load.

From the technical point of view, like results are given by the two methods; the resultant of the effects is a sum or a difference, according as elasticity is brought into play by compression or by tension.

Nevertheless, when the result is a difference the neutral point and the point of inflection do not coincide perfectly, as in the case of elongation followed by contraction; inflection occurs, but is no longer evidenced in such a simple manner as in the case of fractional loads. Heating indeed occurs in the case of small contractions and increasing cooling in the case of large ones, but this is not as a rule distinct. It is preceded by slight heating, the extent of which seems to decrease gradually. This heating would appear to indicate that, at the beginning of all contractions, the contraction of the intermolecular spaces takes place more rapidly than the restoration of the molecules to their equilibrium position.

Chauveau has again observed that, under tension, the elongation increases more rapidly than the load, and that, accordingly, none of the laws governing the elasticity of metals are applicable to rubber, on account of the enormous deformation brought about by a very small force.

Rubber is subject, both in the course of the manipulation which it undergoes during manufacture, and also during the uses to which it is put in industry, to complex mechanical strains, tending to modify its original structure; its behaviour varies greatly from case to case, just as much as the strains themselves vary.

Breuil, in an exceedingly extensive and very complete piece of work,[1] inspired by what had been done in metallurgy, studied the changes in form, and in volume, undergone by rubber under various circumstances. In most instances this investigation could only be carried out with vulcanised rubber, and it therefore does not fall within the limits of our subject, but we feel in duty bound to bring it to the notice of all, on account of the great interest of the subject to those concerned with rubber on the industrial side. Moreover, although it is outside our limits, it is proposed to make use of such matter as relates to, or can be applied to, the case of raw rubber.

It is well known that, in its ordinary form, rubber expands, and expands considerably, when heated. When compressed it heats, and when stretched it also heats, whereas other bodies cool. In the works of Joule, Chauveau—from whom we have just quoted—Villars, Schmulewitsch, and Bouasse much has been said on the subject of these curious phenomena, and the reader is referred to their original memoirs.

Under tension, rubber evidences a singular property which differentiates it clearly from metals subjected to the same method of mechanical analysis. Whereas in the case of metals the elastic deformation follows a definite law—viz., that of proportionality between stress and strain, in the case of rubber no precise law can be deduced from the collected results of experiments. Its deformation is very great, its breaking strain, on the other hand, low, whilst it preserves the characteristic power of recovering its original form, within narrow limits, when the load is removed. From experiments of this character Breuil draws this original conclusion, a curious one, more

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[1] See *Le Caoutchouc et la Guttapercha*, 1904–1905. In the course of these investigations, Breuil made use of a dynamometer of his own invention, one of the most perfect pieces of apparatus for the purpose to be met with.

especially from the point of view of the physical constitution of rubber; he regards pure rubber as an agglomeration of elastic molecules suspended in a medium consisting of a plastic body, as we have already indicated. It is impossible in the present state of our knowledge to give any idea of the proportions in which these two physical components are present, nor of their form and character, but their existence cannot be denied.

Adopting this view, it is easy to understand why pure rubber offers practically no resistance to tension, the reason being that it is a magma of elastic molecules embedded in a cementing medium consisting of an adhesive, soft, plastic hydrocarbon, which can be drawn out like wax, without offering any resistance.

When such a substance is stretched, the deformation will only affect the more malleable constituent, which can be drawn out without effort, dragging with it the elastic molecules, which become elongated also. The deformation will be confined to those places where the cement, the adhesive hydrocarbon, is present in the larger quantity. Hence arise the striæ and the deep grooves to be found on the surface of rubber when a break occurs. In reclaimed rubbers, where the relative proportions of the hydrocarbons has been altered by depolymerisation, and where the adhesive hydrocarbon seems to predominate, Breuil's observations are still more to the point. When this mass is subjected to vulcanisation, as must be done especially in the case of the adhesive hydrocarbon, it then acquires tenacity, loses its malleability, and probably attaches itself more closely to the elastic hydrocarbon. The whole mass becomes homogeneous, and then shares the individual properties of its two constituents.

This is analogous to what occurs in the case of mild steels, which, when they are in the annealed state, give a stress-strain curve with a very gentle slope immediately following the apparent limit of elasticity, but which lose this slope on tempering. This is due to the fact that mild annealed steel is made up of a mass of iron in which are disseminated, in a somewhat irregular fashion, grains of *pearlite*, whilst after tempering it contains nuclei of *martensite*, very small and very close together, which render the mass as a whole more homogeneous.

From these results the great importance of intermolecular phenomena in the case of rubber will be gathered, and it will be easy to understand that, as a matter of fact, it is not enough to have been able to isolate the fundamental hydrocarbon, or its lower polymerides, in order to be in possession of a substance similar to natural rubber.

By varying the conditions of extension, and the temperature of the surrounding medium, a series of curious determinations are to be made. These have formed the subject of a very complete investigation by Bouasse, whose work on this and other subjects is full of remarkably interesting detail. Unfortunately, we are unable to give more than an incomplete account of his results.

Bouasse found that, on varying the speed of extension, the amplitude of the cycles decreases as the speed increases, and that at the same time their form is altered, a slow-speed cycle being broader than a high-speed cycle, the difference residing in the return curves.

If a series of cycles be described between two given loads, with a rest after each extension, it will be found that the elongation gradually decreases as the number of operations increases, whatever be the loads between which the cycles are traced.

If the cycles traced and fixed are of increasing amplitude, the large cycles are found to have a more and more marked influence upon those which follow them—that is to say, the small cycles traced after the test strip has been put through a large cycle, are more inclined to the horizontal than their congeners traced before the large cycle. They are also much narrower. This observation leads to the conclusion that it should be possible to render rubber more elastic, in the narrow sense of the word, by stretching it greatly to begin with, and afterwards only applying to it a lesser tension.

In studying the effect of interruptions upon the form, and the final amplitude of the stress-strain curve of a rubber thread, Bouasse succeeded in showing that loads suddenly applied and kept constant over a certain period produce the same final effect as a series of loads increasing by smaller fractions; his conclusions on this point are identical with those of Chauveau.

Schwarz and Kemp arrived at very similar conclusions in their investigations on "Thermal Phenomena in Rubber."[1]

They state: "The effect of tension upon rubber is to produce a far greater variety of forms than in the case of most other solid bodies. Certain effects which are inappreciable in the latter case become of considerable importance in the case of rubber."

It is possible that the effect of stretching is to rupture certain molecular groupings, producing a change of structure, in such a way that rubber which has been "worked" may well possess very different physical properties from those it exhibited in the unworked state.

Schwarz and Kemp believe that there are two kinds of molecular groupings in rubber. When rubber is subjected to small loads these two groupings behave alike, giving an elongation proportional to the load. But if the latter be increased gradually, one of the groupings is strained to its limit and is consequently ruptured, whilst new molecular aggregates are formed under more stable conditions.

These conclusions are very much the same as, although put in a different way from, those of Breuil upon the dual constitution of rubber, and extremely interesting lessons from the technical point of view are to be learned from this kind of mechanical analysis.

One sees, for instance, that one undeniable result of all the mechanical work of preparation—washing, crushing, mastication, etc.—is to modify the internal structure of rubber, just as stretching modifies it.

On the other hand, a rubber destined for industrial work, a pneumatic tyre, for example, must as a result of this work, and of the heat produced, become completely altered in its molecular groupings and their arrangement. The regeneration of such rubber is, therefore, a difficult matter, because the natural groupings are broken up, and it is necessary to re-form them.

Still other work has been carried out with the idea of formulating concise views as to the mechanical properties of crude rubbers, and their variation.

The one special characteristic of all rubber coagula, of whatever origin, and by whatever method coagulated, is their great irregularity.

There is really nothing astonishing in this. The fundamental hydrocarbon is in suspension in the serum in the form of globules, the material of which may vary, although maintaining the empirical composition C_5H_8 or $C_{10}H_{16}$, in the same way as turpentines of different origins vary. These globules are in equilibrium in the serum, as explained by Gardner, and this

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[1] *Le Caoutchouc et la Guttapercha*, 1911, 8, 5293.

is subject to the same influences on the part of the plant. Coagulation, according to Boutaric,[1] seems to be a disturbance of this equilibrium from any one of a great variety of causes, resulting in new, more or less perfect, and more or less stable, structures, endowed with chemical, physical, and mechanical properties which perforce vary.

It is quite natural, then, to find, on examining the tensile strength and elongation of different rubbers, that these properties are subject to very great variation. The following table, which has been drawn up by Boutaric, furnishes interesting information on this subject. A represents the elongation at break of a strip 100 mm. long, R the tensile strength per square mm. of cross-section. C is the product (A × R) ÷ 2,000. The figures given are the mean values obtained from twenty experiments :—

KIND OF RUBBER.	A.	R.	C.
	Mm.	Grm.	
Brazilian Para, ...	842	1,354	570
Plantation Para, ...	840	1,339	562
Manaos Sernamby, ...	820	1,200	492
Maniçoba, ...	820	920	377
Peruvian Sernamby, ...	930	750	348
Caucho, ...	910	720	327
Niggers, ...	1,040	700	364
Twist, ...	960	670	322
Indo-China, ...	1,010	490	247

The following table is sufficient to indicate the wide variation in tensile strength and elongation which may be brought about by coagulating one and the same latex by different methods :—

METHOD OF COAGULATION.	A.	R.	C
	Mm.	Grm.	
Heat and evaporation at 80° C., . .	610	170	51·5
Evaporation at 25° C., ...	500	190	47·5
Concentrated acetic acid, . . .	710	210	74·5
Trichloracetic acid, washed, dried, . .	600	325	97·5
Acid + a salt, ...	530	310	82·1
Weak acid + 2 salts, ...	560	490	137·2
Strong acid + 2 salts, ...	620	660	204·5

Besides the influence which "tackiness"—a defect to which rubber is liable, and which we shall consider later on—may have upon tensile strength, there are other circumstances which may help to explain these very great variations amongst different rubbers and different coagula from the same latex.

Boutaric has put forward a hypothesis on this subject which from some points of view closely resembles that which is supported by Seeligmann and by Breuil, chiefly in the assumption of the presence in ordinary rubber of two distinct constituents, the one plastic and the other elastic. Boutaric's view is that there exists for the hydrocarbons $(C_5H_8)_n$, of which rubber is

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[1] *Le Caoutchouc et la Guttapercha*, 1911, 8.

made up, a state of maturity, and that certain of these hydrocarbons which have not yet reached this state are in suspension in the serum, and on coagulation are carried down with the soft hydrocarbons. When the rubber containing them is subjected to mechanical treatment or to heat, they soften or melt and dissolve the softer hydrocarbons by which they are surrounded. The result is a diminution of tensile strength, and the hypothesis thus affords an explanation of the anomalies in the two tables given above.

Without going into the details of investigations on compression, it is necessary to note the following points :—

1. The reversibility or recovery of rubber under compression is not perfect;

2. There is analogy between the results of stretching and of compression tests; the curves in the two cases are analogous, although not alike, for on extension great deformation is produced by small loads, whilst the reverse is the case on compression.

The plasticity of rubber has formed the subject of a number of researches, including those carried out by Gerber.

Plasticity plays an important part in the treatment of rubber in the factory, for it is this property which determines how the rubber must be worked, and to what uses it can be put. When a washed raw rubber enters the process of manufacture it is subjected to a vigorous working between rollers, the effect of which is to heat it and render it plastic; but this purely mechanical process destroys a number of the properties of the rubber, modifying its physical characteristics and reducing its elasticity. Experience has shown that the desired degree of plasticity is reached the more rapidly according as its natural plasticity is the more pronounced, it is therefore of great interest to be able to define and measure this characteristic with the greatest possible precision.

In this connection Gerber measures plasticity by observing the time in seconds taken by a needle loaded with 40 grammes per sq. mm. to penetrate to a depth of 1 mm. into a block of washed, dried rubber, which has been compressed hydraulically, and which is maintained at a temperature of 100° C. in a glycerine bath. He has obtained the following figures :—

KIND OF RUBBER.	PLASTICITY.		
	Maximum.	Minimum.	Mean.
Brazilian Para, ...	236	56	102
Manaos Sernamby, ...	...	...	40
Ceylon, 1st and 2nd Grades, . . .	108	21	50
Ceylon, 3rd Grade, ...	45	25	34
Plantation Sernamby, ...	...	...	40
Maniçoba, ...	52	23	35

In the same connection a very ingenious little apparatus was devised, in 1908, by Breuil, to whom the rubber industry is indebted for so many services. With this apparatus, which is termed the *elastodurometer*, the elasticity and the hardness or plasticity of any rubber can be measured at the same time.

The measurement of elasticity is based upon the following principle :—

If a hard—*i.e.*, a non-deformable—steel ball be allowed to fall from a given height upon a flat sheet of rubber, which is held down in such a way as not to be displaced by the blow, the ball will rebound to a height which will vary in proportion to the elasticity of the rubber. The ratio of these two heights to one another will be a measure of the elasticity of the rubber.

Plasticity or hardness is measured on the same principle as applied by Gerber—viz., the penetration of a steel point into a block of rubber of a given thickness and prevented from moving. The load necessary to cause the steel point to penetrate to given depth measures the resistance, or rather the plasticity of the rubber, and is itself measured by means of a dynamometer. In Gerber's apparatus the time is taken as a measure of plasticity, the load and depth of penetration remaining constant; in Breuil's apparatus the load is taken as a measure of hardness.

In measurements of elasticity the ratio of the height of rebound to the height of fall, $h_r : h_c$, scarcely ever exceeds 60 per cent., which means that 40 per cent. of the work done on the rubber is absorbed, the reversibility of the deformation suffered being far from complete.

Breuil's *elastodurometer*, which has been improved in several directions by the inventor, enables the uniformity of elasticity of a tyre, or of any other manufactured rubber article, to be verified very easily.

The following figures have been obtained for the elasticity of various crude rubbers. The height of fall was 250 mm. in each case :—

KIND.	REBOUND.	$h_r : h_c$.
	Mm.	Per cent.
Tamatave Pinky, . .	170	68
Manaos Sernamby, . .	100	40
Sudan Niggers, . . .	135	54
Madagascar Twists, . .	130	52

Lowering the temperature of rubber produces certain curious effects, which have been studied by Terry and by Boutaric.

One of the applications of this branch of investigation does not come within the scope of this work; we refer to the manufacture of cut-sheet—"Feuille Anglaise"—which, therefore, we only mention in passing.

According to Terry, rubber is very sensitive to changes of temperature, a fact which had been pointed out by Fresneau in the eighteenth century; for instance, if heated to a temperature near to its point of decomposition it cannot be solidified again. There is clearly, in this case, depolymerisation, although the action has not yet been fully explained.

Claude states that at the temperature of liquid air rubber becomes as brittle as glass, but even this intense cold does not bring about any kind of depolymerisation, the rubber recovering its elasticity completely on reverting to the normal temperature.[1]

In the process of washing, drying, and mastication, coagulated rubbers are subject to numerous thermal influences, the result of which is to modify

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[1] It would appear that between these two extreme thermal effects—congelation and decomposition—there ought to be a point at which a state of perfect equilibrium of a normal rubber exists. This point has not been determined thermometrically.

them in some way; the actual effect appears to consist in a molecular simplification, resulting from increased temperature.

The course of such changes can be well followed by means of viscosity measurements, and to this subject we shall turn our attention later on. Thus, if the viscosity of a rubber masticated for ten minutes be determined by Boutaric's method and found to be 150, for example, it might be found that, after the same sample had been put through the further process of calendering its viscosity was reduced to 100.

The following figures have been obtained with vulcanised samples of rubber masticated for different lengths of time; the test pieces were all of the same thickness. The results are suggestive:—

KIND OF RUBBER.	Time of Mastication.	Elongation (A).	Breaking Strain (R).	Product $\frac{(A \times R)}{2,000}$.
	Minutes.	Mm.	Grm.	
Para, ...	30	820	1,400	574
	60	810	1,100	445
Congo, ...	20	1,020	700	357
	40	925	400	185

These figures indicate the order of magnitude of the differences observed, and also show that the phenomenon is common to rubbers of different origin, and is more marked in the case of the lower grades than with the best.

The question arises as to whether it is possible for a rubber, the properties of which have been modified in this way, to be restored to its original state under the influence of low temperatures, somewhat in the same manner as a faulty coagulation can be rectified by the addition of a new electrolyte. The idea is conceivable, assuming the change to be brought about solely by the influence of heat; but if other causes contribute, it is rather unlikely that refrigeration will do more than effect an improvement, and that it will bring about complete recovery.

Some light is thrown upon this subject by the work of Bouasse.[1]

All mechanical manipulation of rubber, more particularly of raw rubber, leaves its stamp upon it in the form of some internal transformation or deformation, which is partly of a permanent character, having no definite limits, and shows itself more particularly in *hysteresis*. The same is true of the action of a physical agent such as heat. These actions are two-fold, part of their effect being instantaneous, and part gradual. Low temperatures appear to affect only the slower portion; the result of refrigeration can, therefore, only be partial.

The effect of heat upon rubber, even at very moderate temperatures, such as + 15°, + 20°, or + 40° C., maintained for a considerable time, is to bring about a very marked reduction of strength. Rubber which has been vulcanised, and is, therefore, under the best possible conditions, passes first of all through a maximum and then follows a descending curve leading it slowly but surely towards decay.

Some figures given by Boutaric are very instructive on this point:—

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[1] *Ann. de la Faculté de Toulouse*, 1903–1904.

EFFECT OF HEAT ON RUBBER.

SAMPLE.	Elongation (A).	Breaking Strain (R).	Product $\frac{(A \times R)}{2,000}$.
	Mm.	Grm.	
Kept 5 days after vulcanisation at +45°C.,	880	920	405
,, 6 ,, ,, ,,	870	1,020	444
,, 36 ,, ,, ,,	660	480	158
,, 6 months ,, ,, { +15° to +20°C.,	680	700	238

We are in ignorance as to the mechanism of this degradation, but it has been shown that if samples of the same rubber be kept for the same length of time at different temperatures, the extent of degradation is proportional to the temperature, and that at temperatures below 0° C. it approaches zero.

Breuil,[1] whose work on the mechanical investigation of rubber—carried on with the aid of his own special dynamometer—is well known and appreciated, has also turned his attention to the micrography of rubber, a subject which he has designated, very picturesquely, as "*gomographie.*"

Just as it is impossible to judge a wine on its chemical analysis alone, so it is with rubber, and it is precisely this fact which makes Breuil's work in this connection interesting in the highest degree.

Analysis, in fact, cannot give any information upon the internal organisation of the substance, cannot tell us if the constituent elements are distributed uniformly within it, or what are their relative positions.

The vaguely descriptive term " nervous " is hardly sufficient to characterise a rubber; is it not probable that the secret of its physical properties, on which its technical value depends, would be revealed, if the intimate structure of the rubber could be laid bare? Just as the application of the microscope to the study of metallurgical products has yielded a rich harvest of valuable knowledge, so its employment in the examination of various rubbers may be equally fertile in instruction.

Up to the present, obviously, the results obtained have only been scanty, but they are sufficient to show that the solution of the problem is by no means impossible.

Without going into details as to methods of observation, and a description of the modifications which Breuil found it necessary to introduce in the microscope to make it suitable for rubber research, we propose to summarise his results.

Breuil had hoped that, as in the case of the colloids investigated by Quincke, rubber solutions prepared under identical conditions would, when dried off on a microscope slide, yield films differing in constitution, or arrangement, in different species.

This hope was not realised. Under high magnifications (at least 300) it is observed very clearly, as the solvent evaporates, that particles of rubber are in rapid movement, and that they join up with one another in such a way as to produce a network with large cellular meshes, which spread out and finally disappear.

This observation in the case of solutions is, therefore, much less definite than that made by Victor Henri with dialysed latex.

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[1] *Le Caoutchouc et la Guttapercha*, 1905, 2, Nos. 3, 4, 5, 6.

But although the method of solutions yielded, in Breuil's hands, no precise information in the case of rubber, when he extended the method to guttapercha—which is, after all, only a rubber with a low degree of polymerisation—he was able to observe the very distinct formation of a network, from a solution in carbon disulphide.

Nevertheless, in comparing solutions of the same rubber vulcanised and not vulcanised, Breuil found that the raw rubber gave identical ramifications in all solvents, whereas although the vulcanised rubber also gave networks, these were unlike each other, and were unstable.

By making use of modifications in lighting, by employing Kohler's photographic method with ultra-violet rays, and by applying Cotton and Mouton's ultra-microscope, Breuil and Boutaric have obtained very interesting results, especially from the point of view of vulcanised rubber, for they have been able in this way to study the diffusion of sulphur through rubber. But these points do not come within the scope of this work, and we must refer the reader to Breuil's own interesting paper on the subject.[1]

We have only one further remark to make in this connection; the cellular structure of rubber revealed by this means shows it to be a non-compact body, with internal lacunæ, and the curves displaying the results of dynamometric experiments are in perfect agreement with this conclusion.

Both Chauveau and Breuil, when expressing dynamometric results in the form of curves, find in the latter long bends or " points " of inflection, followed by a straight line slope, as has also been observed in the case of ropes; an explanation of this lies in the assumption that in the earlier stages of the stretching process, the material with its lacunæ—a sponge-like structure—is much altered in shape by a very moderate pull, but that when the opposite walls of the cells or lacunæ are very close together it is only the material itself which is deformed, behaving thus as a compact substance, which is only slightly deformed by a large load, up to its elastic limit.

Schidrowitz has also investigated the structure of raw rubber.

Black rubber, cut into sections by means of the freezing microtome, exhibits under the microscope the structure common to many organic *gels*—viz., that of an open network, or fine sponge.

Schidrowitz found that by vulcanising with sulphur chloride this structure could actually be made out. Under a magnification of 200 diameters *Hevea* and *Funtumia* rubbers, in thin section, are seen to contain numerous globules, and this is also true of benzene solutions when examined with the ultramicroscope.

The globules are less visible in the more transparent films than in the more opaque, and vulcanisation with sulphur chloride increases their visibility.

In brief, Schidrowitz concludes that the globules are not destroyed by the coagulation of latex, nor by solution in benzene, but that they continue to exist under these conditions, in their original form.

Light appears to have a detrimental influence upon raw rubber, inducing a number of changes in it; together with heat, it is the most active agent in bringing about deterioration. The action of light, and in particular of the ultra-violet rays, has been investigated by Victor Henri,[2] who exposed various samples, at short distances, to the rays from a mercury vapour lamp, for some forty hours.

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[1] *Le Caoutchouc et la Guttapercha,* 1906, 3, 200.

[2] *Le Caoutchouc et la Guttapercha,* 1910, 7, 4371.

The use of the mercury vapour lamp has enabled changes which would take weeks or even months to show themselves with ordinary light to be detected in a comparatively short time; the action of visible and of ultraviolet light is the same, but proceeds at a higher velocity in the latter case.

Henri found that after twenty hours' exposure the surface of the films of rubber under examination became more glossy and darker in colour, and on stretching the films small cracks developed on the surface.

With more prolonged exposure this action of the ultra-violet rays became accentuated; the surface of the film became covered with cracks, the colour became redder, and the rubber tacky; finally it lost all its strength and elasticity, and tore as soon as it was stretched. While this result is brought about within forty hours in the case of raw rubber, vulcanised rubber requires nearly double the exposure before showing similar marked deterioration; the latter is, therefore, much more resistant to light action than the unvulcanised substance.

Raw rubber recovered from its solutions in benzene, and, therefore, already suffering from deterioration in some of its physical properties as the result of depolymerisation, is destroyed by the ultra-violet rays in less than twenty hours. The films become very brown and crumble to pieces, or become sticky.

The question arises as to whether this action is of a purely physical character, or whether light acts by determining the production of ozone in the atmosphere, and thus a chemical action on the rubber.

It was found that when samples of the rubbers used in the experiments just described were sealed up in vacuous glass tubes and exposed for the same length of time to ultra-violet light there was no deterioration. The conclusion may, therefore, be drawn that the action of light upon rubber is indirectly a chemical action, and that the deterioration of the rubber is due mainly to partial ozonisation. That being so, and putting Harries' experiments alongside those of Victor Henri, it should be possible to isolate products of the action related to levulinic aldehyde, but no experiments have been made in this direction.

Henri states, again, that it is very difficult to obtain analytical results which throw any light upon these photolytic oxidations, for the very good reason that the change undergone by the rubber is of a very irregular character. Whereas the surface layer is almost completely decomposed, the subjacent and lower layers are not appreciably affected.

The change could probably be carried to completion by prolonging the exposure, and turning the sample over. But if the change is due to ozonisation we know that the final products are either levulinic aldehyde, or its peroxide, or levulinic acid, each of which is a substance easy to detect; the experiment could, therefore, be readily carried out. On the other hand, by acting on a certain mass, it would be possible to isolate the successive products of the reaction, and thus to arrive at its mechanism. This is a matter of sufficiently great importance from the technical point of view to warrant the pursuit of experiments in this direction. When studying the absorption of the violet rays by rubber, Victor Henri found that sheets of rubber, of a clear yellow tint, obtained by the evaporation of dialysed latex, are transparent to the ultra-violet rays up to a wave length of 3,650. There is slight absorption up to 3,341 or even 3,125, and the remainder of the spectrum, from 3,125 to 2,302 is completely absorbed.

The whole of that end of the spectrum is, therefore, active towards rubber, and it is easy to understand that under these conditions such changes as oxidative decomposition, molecular fission, and depolymerisation may occur, facilitated by the catalytic influence of the impurities in the rubber.

The net result of Henri's work is to demonstrate, incontestably, that light has a destructive action upon raw rubber, and that it is the more refrangible rays which are the most active in this connection.

In order to prevent this destructive action it is necessary to keep this still unvulcanised rubber away from the influence of photo-chemical radiation, and this is done, empirically, by keeping it in dark, well-ventilated stores. But certain precautions must also be taken in view of transit, and package in yellow paper, or in wooden cases of a yellow colour, in order to absorb the ultra-violet would seem to be advisable.

While on the subject of the deterioration of rubber, we are led logically to refer to the curious phenomenon of *tackiness* or *stickiness* in rubber. Under certain circumstances raw rubber is subject to a spontaneous loss of "nerve," and to a kind of liquefaction, by which it is converted ultimately into a black, viscous, sticky mass.

This change was formerly attributed either to a defective method of coagulation, or to the presence, in the mass of rubber, of bacteria, which brought about a particular kind of fermentation.

Bertrand's investigations[1] tend to show that this view is erroneous, and that the change which occurs is rather of a chemical character, and is determined by the action of heat and light on certain kinds of rubber.

In addition to these physical factors, the botanical origin of the rubber plays a great part; for whereas certain African rubbers are very subject to tackiness, other grades, such as *Hevea* rubbers, either wild or cultivated, are never troubled with this complaint.

The first hypothesis of fermentation was the one which came naturally to the mind. It is, in fact, very easy to understand how the process of coagulation, and the mode of preservation of the rubber, may either assist or inhibit fermentation.

Latex contains not only globules of hydrocarbons and resins, which unite on coagulation, but also a watery serum, holding in solution mineral and organic salts, sugars, and protein. This highly fermentable liquid remains imprisoned in small vesicles in the rubber. If heat or antiseptics have been employed in coagulation, the bacterial flora is destroyed, and there is little danger of the imprisoned liquid fermenting. But if, on the other hand, coagulation has been carried out at ordinary temperatures, without antiseptics, or, worse still, if substances such as urine have been added to the latex (as is often done in Africa), the development of numerous micro-organisms—bacteria or moulds—is only to be expected.

Thorough drying, and a low temperature check fermentation; dampness and moderate heat, on the other hand, hasten it.

It is not so easy to see how the method of coagulation can modify the very nature of the raw rubber, to the point of rendering it unstable when it is not naturally so. Thus there has been a disposition to regard tackiness as of microbial origin.

As already pointed out, all rubbers are not equally liable to develop tackiness; it occurs more particularly in the African sorts, which are coagu-

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[1] *Le Caoutchouc et la Guttapercha,* 1908, 5, 1942; 1909, 6, 3216.

lated by a great variety of methods, and, as a rule, without great care. When we compare these primitive methods with the smoking process, which both dries and antisepticises the rubber, and when we find that Brazilian rubber prepared in this way is exempt from the ravages of tackiness, it is natural to draw the conclusion that coagulation is the determining factor in this particular species of deterioration.

But experiment has shown that even when the Amazonian methods are applied to African rubbers, and even when large quantities of antiseptics are added to the coagulants, deterioration is not prevented, whilst the Brazilian scrap rubbers, such as negroheads, which have not been smoked at all, nor received any antiseptic treatment, are practically immune.

It follows from these observations that if tackiness is the result of a transformation induced by bacteria, all rubbers are not subject to it, and that, consequently, the botanical origin of the rubber must be taken into account.

According to Hugot, this disease is contagious, and one infected spot is sufficient to contaminate a whole parcel. The spread of the contagion is hastened by the presence of moisture, and by exposure to sunlight. Under the latter influence advanced tackiness is brought about, according to Hugot, in a few hours; according to Brindejonc, in two hours.[1]

Putting these considerations side by side with Victor Henri's work on the action of light, and with what we know about depolymerisation under the influence of heat, since bacteria—as shown by Downes, Duclaux, Roux, Arloing, and Buchner—are destroyed by sunlight, it does not seem possible to attribute such action to them. The determining cause is rather to be sought for in the combined influence of heat and light, upon a substance in a state of imperfect molecular solidity or polymerisation.

If, on the other hand, the action were bacterial in character, it could only take place slowly, at all events at first; several days would be necessary to allow a sufficient number of germs to develop to bring about any appreciable change. But when all the proportions are adhered to the action is almost instantaneous. We have seen that the action of light, especially upon rubbers which are already partly depolymerised, is very rapid, and we know, on the other hand, from Daniel Berthelot's work, that the presence of catalysts reduces, to a very considerable extent, the time required for the ultra-violet rays to have their effect. The rôle of the impurities in certain kinds of rubbers which are predisposed to becoming tacky—in particular, the salts of magnesia—may possibly be of this order. In the present state of our knowledge one is very much inclined to believe this.

Bertrand rejects completely the idea of attributing this curious phenomenon of tackiness to bacterial fermentation. He regards it as an irresistible molecular transformation, brought about by physico-chemical influences, amongst which light and heat play the chief part, but are aided by the co-ferments discovered by Spence. But according to Bertrand the chief factor in this decomposition is the botanical origin of the rubber.

With good show of reason Bertrand maintains that there is latex and latex, just as there is essence and essence. Essence of lavender and essence

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[1] Other influences prior to coagulation may also play a part; thus Spence has observed that coagula from the same latex, a portion of which had been heated with 0·1 per cent. of sulphuric acid, differed from one another. The coagulum from the sulphuric latex is tacky and sticky; whereas the other is firm and nervy.

of lemon contain different substances; *Euphorbia* latex contains resins, and *Hevea* latex contains rubber.

The comparison may be urged still further. The Siberian pine produces an essential oil; but, in addition to pinene and sylvestrene, bornyl acetate in considerable quantity is also found in it. In French turpentine, an unsaturated hydrocarbon of the empirical formula $C_{10}H_{16}$, various isomerides are found, differing from one another in one or more properties, such as smell, rotatory power, boiling point, susceptibility to oxidation, readiness to form compounds—solid or liquid—with the halogen acids. May it not also be the case that rubber contains a number of different isomerides?

The discovery of abnormal rubbers, and the different kinds of molecular grouping which are there met with, lends some support to this hypothesis. In such a case there might well exist stable isomerides such as those found in *Hevea* latex, and others present in African grades, which have the unfortunate liability to tackiness.

The difference between these two types does not depend upon the method of collection or of coagulation, but upon their botanical origin—that is to say, upon the species of plant from which they are obtained. Light and heat constitute the impulse which causes the phenomenon to display itself.

Bertrand has drawn up the following list of rubbers which are liable to tackiness, based upon samples in the Museum, the École de Pharmacie, and the Jardin Colonial:—

LIABILITY OF RUBBERS TO "TACKINESS."

Euphorbiaceæ—		
Hevea,	Peru Sernamby,	Very slightly tacky.
,,	Guiana,	,, ,,
,,	Cameta,	,, ,,
Manihot,	Ceara,	,, ,,
Intisy,	Fort Dauphin,	,, ,,
Artocarpeæ—		
Castilloa,		Tacky.
Ficus elastica,		,,
,, prolixa,		,,
Asclepiadeæ—		
Marsdenia verracosa,		,,
Apocynaceæ—		
Hancornia,		,,
Gohina,		Very slightly tacky
Landolphia owariensis.		
,, vœahena,		Tacky.
,, piralahy,		,,
,, sphærocarpa,		,,
,, Gallieni,		,,
,, subsessilis,		,,
Funtumia,		,,
Ecclysanthera (Laos),		,,
Xylinataria (Tonkin),		,,
Microchytes (Annam),		,,
Other families—		
Parthenium argentatum,		,,
Lobelia,		,,
Vahea Senegalensis,		,,
Bleekrodea (Tonkin),		,,

Since rubber forms pseudo-solutions with various solvents, it is useful to speak of its viscosity, which has in recent years been the subject of many investigations. It has indeed been put forward as the basis of a rapid method of determining the commercial value, or the "nerve" of a rubber.

The idea of studying the viscosity of rubbers seems to have first occurred to Axelrod,[1] who, working with benzene solutions, observed the time taken by 100 c.c. to flow from a containing vessel. The ratio of this figure to 4·5 he called the viscosity of the solution.

Axelrod held that as the rubber resins are insoluble in benzine—an incorrect supposition—their presence does not affect the viscosity. The following are some of the viscosities found by Axelrod:—

VISCOSITIES OF CERTAIN RUBBERS.

Concentration of Solution.	Fine Para.	Ceylon.	Congo.	Para Hard Cure.	Peruvian.	Bolivian.	Borneo.
Per cent.							
3	6·0	2·7	2·2	3·4	...	...	2·6
4	79·3	6·2	5·3	12·9	2·4	2·0	6·2
5	63·3	15·5	11·3	52·2	5·5	3·5	16·7
6	...	32·0	28·2	107·3	12·9	6·2	44·0
7	...	60·7	62·2	...	28·2	12·6	101·5
8	...	116·17	132·2	...	47·8	26·7	171·1
9	...	160·0	...	...	87·5	43·0	...
10	...	...	...	...	...	66·7	...

According to Axelrod, the curves expressing these results are parallel from a certain point onwards:—"The curves obtained by plotting the logarithms of these viscosities (as one co-ordinate) cut the horizontal at an angle tan^{-1} 5 in every case. If the viscosity of a solution be represented by V, and its concentration by p, the relation between viscosity and concentration is represented by the equation—

$$V = C p^r,$$

where C is a constant determined by the quality of the rubber, and r the tangent of the angle which the curve makes with the horizontal. r being found, it is easy to calculate C, and knowing C, the consistency of the solution at a given concentration can be calculated, or conversely."

Axelrod proposed at that time to apply this method to the evaluation of rubbers. Schidrowitz, and later Frank, took up this question again, and Frank put before the International Rubber Testing Committee a viscometer, evidently inspired by the first apparatus constructed by Axelrod.

Frank employed as solvent, xylene, having a density of 0·867 at 15° C., and boiling between 135° and 140° C., and his solutions contained 3 per cent. of dry rubber. The apparatus was standardised with pure glycerin, of density 1·25 (30° Beaumé), the time taken by 100 c.c. of the liquid to flow from the orifice being noted. Measurements were made, first with the freshly prepared solutions, and secondly with the same solutions after keeping them for 8 to 10 days in the dark.

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[1] *Le Caoutchouc et la Guttapercha,* 1906, 3, 559.

In this way it was observed by Marckwald that at the end of this time solutions of medium-grade rubbers became cloudy, and deposited solid matter.

Viscosity determinations do not seem likely to yield the good results which were expected of them, owing, more particularly, to the great effect which mastication of the rubber has upon the magnitude of this constant.

According to Boutaric, a Ceylon Para rubber which, before mastication, gave a 2 per cent. benzene solution with a viscosity of 2,000, after mastication for various lengths of time gave the following results :—

TIME OF MASTICATION.	VISCOSITY.
2½ minutes, ...	1,900
5 ,, ...	540
10 ,, ...	150
15 ,, ...	110
20 ,, ...	90

On the other hand, it is known, from Victor Henri's experiments, that a protracted drying process affects the solubility of rubbers in various solvents to a noteworthy extent. With such variations to contend with, it is obvious that results obtained by Frank's process will have only a comparative value, since it will never be possible to deal with rubbers in a mathematically identical condition.

With a similar idea, Victor Henri suggested another method by which the viscosity of a solution can be estimated very rapidly. The method consists in sinking a calibrated tube in the solution to a certain depth, and measuring the time taken by it in rising through the distance between two marks. The unit is the time taken when the pure solvent is used.

Another method was proposed by Boutaric, which consisted in measuring the time taken by a ball in falling through a column of the solution of a given height, contained in a graduated test-tube.

Neither Pontio, whose authority in matters relating to the analysis of rubber is admitted, nor Breuil lend their support to these suggestions, the object of which is to judge of the value of a rubber by a knowledge of its viscosity. Pontio says, for example,[1] that a certain quality which by analysis contains only 80 per cent. of rubber, may have a viscosity equal to that of first-grade Para containing 96 per cent. The character of the resins present, for example, in certain tacky rubbers, is such as to increase the viscosity instead of reducing it.

Although it may be true that, for certain qualities of rubber, a relationship can be established between the rubber content and the viscosity, this does not hold true for all rubbers, and it is not possible to conclude that because a rubber gives a certain percentage figure on analysis the viscosity will be proportional to this figure. In such a case impurities play a part which cannot be overlooked.

Schidrowitz and Goldsbrough [2] have attempted to establish a relationship between the "nerve" of a rubber and the viscosity of its solutions.

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[1] *Le Caoutchouc et la Guttapercha,* 1911, 8, 5108.

[2] *J. S. C. I.,* 1909, 28, 3.

Their experiments showed that such a relationship does appear to exist, but that it is not direct, " nerve " being determined by two different factors, one of a mechanical nature, the other chemical (polymerisation).

Schidrowitz employed the Ostwald viscometer, using 1 per cent. benzene solutions, and the viscosity was calculated in relation to that of benzene as unity. The rubber content of the solution was determined by evaporation at the conclusion of each experiment.

The following results were obtained :—

KIND OF RUBBER.	CONCENTRATION.	VISCOSITY.
	Per cent.	(Benzene = 1.)
Funtumia, No. 1, . . .	1	19·1
,, ,, 2, . . .	1	35·3
,, ,, 3, . . .	1	27·3
,, ,, 4, . . .	1	37·0
,, ,, 5, . . .	1	16·6
Hevea, Plantation, No. 1, . .	1	6·7
,, ,, ,, 2, . .	1	9·3
,, Brazilian, . . .	1	26·2

When viscosity-concentration curves are plotted they are found to become straight lines at a certain viscosity. This point may be termed the critical point, and beyond it viscosity is directly proportional to concentration. Extrapolating for 100 per cent. solutions, Schidrowitz obtained the following theoretical values for the viscosity of the pure rubbers :—

Funtumia, No. 1, . .	4·966	Hevea, Plantation, . .	1·400
,, ,, 2. . .	8·946	,, ,, . .	1·400
,, ,, 3, . .	7·551	,, Brazilian, . .	7·253
,, ,, 4, . .	9·343		
,, ,, 5. . .	9·940		

For the sake of comparison, Schidrowitz made mechanical tests, and obtained the following results :—

RUBBER.	Elongation.	Breaking Strain.	Coefficient of Resiliency.	Viscosity.
Hevea, Plantation,[1] . .	9·75	218	57	8·843
,, Brazilian, . .	10·00	406	75	7·253

The indications of the viscometer were obviously of more or less comparative value from the point of view of the determination of elasticity, but no great confidence could be reposed in them.

Bouasse has devoted his attention to the determination of the coefficient of expansion of rubber. This problem is of great industrial interest, but, generally speaking, one cannot, as in the case of metals for instance, arrive at a simple value, and for these reasons :—

(1) The great diversity amongst rubbers.

(2) The influence of working and other external circumstances upon the physical condition of rubber.

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[1] From a 30-year old tree, very strong.

In dealing with rubber, it is never the same physical entity that is dealt with in any two successive operations.

We regret that we cannot reproduce the very remarkable memoir by Bouasse[1] in its entirety, but in it he gives the following as the most rational way of defining the coefficient of expansion :—

Under a constant load, P, a series of changes is gone through from T degrees to T + Δ T degrees, and from T + Δ T degrees to T degrees. Gradually successive cycles become identical; in other words, the lengths L and L + Δ L corresponding to the limits of temperature, T and T + Δ T tend towards certain definite values. Then, the *coefficient of expansion at constant load* for the length L, temperature T, and load P is given by the expression—

$$\beta = \frac{1}{L} \cdot \frac{\Delta L}{\Delta T}.$$

The length L is now kept constant, and a series of temperature changes from T to T + Δ T and from T + Δ T to T is carried through; gradually successive cycles become identical; in other words, the loads P and P + Δ P, corresponding to the limits of temperature T and T + Δ T, tends towards certain definite values. Then, the *coefficient of expansion at constant length* for the length L, temperature T, and load P is given by the expression—

$$\gamma = \frac{1}{P} \cdot \frac{\Delta P}{\Delta T}.$$

There is nothing to indicate that these coefficients β and γ will be independent of previous operations, or that they will always be the same for the same values of P, L, and T.

Although, as a colloid, rubber has no definite melting point, and values given for this constant cannot be used as a means of identification, Ditmar has studied this question in the case of certain sorts of which he had previously determined the resin content, with a view to ascertaining the influence of the latter upon the melting point.

In order to avoid contact with air, Ditmar worked with a thermometer to the bulb of which he attached the sample under examination, and which was then placed inside a stoppered glass tube and heated in a sulphuric acid bath.

The following results were obtained :—

INFLUENCE OF RESIN CONTENT.

Kind of Rubber.	Observations during the Determination.	Melting Point.	Resin Content.
		° C.	Per cent.
Para, fine, ...	Brown colouration at 170° C., . .	188	1·44
,, extra fine, . .	,, ,, 160° C., . .	170	3·57
Castilloa, . . .	Soft and sticky at 170°, firm at 200°, black at 210°, soft at 220°, decomposes at .	220	3·12
Hancornia, . . .	Soft and sticky at 80°, ...	125	9·6
Landolphia owariensis, .	Soft at 145°, but not sticky, porous and black at 160°, sticky at 240°, decomposes at	244	12·23

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[1] *Le Caoutchouc et la Guttapercha,* 1911, 8, 5288.

INFLUENCE OF RESIN CONTENT—*Continued.*

KIND OF RUBBER.	OBSERVATIONS DURING THE DETERMINATION.	Melting Point.	Resin Content.
		° C.	Per cent.
Landolphia, Mozambique,	Blackens at 140°, porous at 200°, sticky at 220°, decomposes at	228	8·62
,, large balls,	Soft at 150°, black and porous at 200°, sticky at 224°, decomposes at	245	11·23
,, spindles,	Blackens at 140°, soft at 160°, black and porous at 200°, decomposes at	248	6·8
,, , Manaï,	Dark at 120° soft and sticky at 220°, decomposes at	235	4·4
Gambia balls,	Soft and sticky at 30°, colour unchanged, melts at	100	3·4
Landolphia, Cameroons,	Unchanged at 100°, black, sticky, porous at 210°, decomposes at	230	5·99
Manihot,	Heterogeneous at 170°, brittle at 220°, decomposes at	246	6·81
Landolphia, Madagascar,	Brittle at 200°, sticky at 220°, decomposes at	242	3·39
,, Nigger,	Hard at 170°, soft and sticky at 175°, decomposes at	224	3·94
Soudan twist,	Soft and sticky at 145°, darkens at 180°, decomposes at	230	7·99
Ficus, Borneo,	Soft and sticky at 146°, firmer at 200°, decomposes at	218	4·76
Fine Ceylon Para,	Sticky at 190°, slightly discoloured, melts without decomposition at	228	2·26

With washed rubbers the following results were obtained :—

INFLUENCE OF RESIN CONTENT (WASHED RUBBERS).

KIND OF RUBBER.	OBSERVATIONS DURING THE DETERMINATION.	Melting Point.	Resin Content.
		° C,	Per cent.
Para,	Sticky at 180°, decomposes at	190	3·98
Dead Borneo,	Soft at 60°,	85	75·62
Guayule,	,, 116°, decomposes at	118	21·31
Uellé,	,, 132°, ,,	144	8·10
Lumps,	Discolouration at 120°, sticky at 150°,	166	26·64
Bassam,	,, 125°, ,, 150°,	168	13·33
Congo,	,, 120°, ,, 160°,	180	7·87
Kinsembo,	,, 120°, ,, 158°,	170	4·78
Congo thimbles,	,, 115°, ,, 135°,	146	7·79

Except in the case of Dead Borneo, the melting point does not appear to depend upon the resin content ; it is related, more particularly, to the quality of the rubber—that is to say, to its botanical origin and mode of coagulation, which influence its degree of polymerisation.

On the other hand, it will be noticed that most of the rubbers, even the medium grades, are able to stand heating to the temperature of vulcanisation—130° to 135° C.—without melting. The melting points of the best grades lie between 185° and 230° C.

CHAPTER IX.

CHEMICAL ANALYSIS OF COAGULATED RUBBER.

Having considered—perhaps in somewhat lengthy fashion, although our motive in this has been explained—the physical properties of coagulated rubbers, we propose now to deal with the question of their chemical examination.

In order to conduct a thorough investigation of this sort, it is first of all necessary to get the rubber into solution, an operation which, because of the colloidal nature of rubber, is not always of the simplest character. In fact, rubber forms with solvents only *sols*, or pseudo-solutions, which are almost unfilterable, and from which the really insoluble impurities, such as the proteins, cannot, therefore, be easily separated.

However, as the result of patient investigation, extending over more than a century, and carried on successively by Fresneau, Macquer, Hérissant, Weber, Harries, Pontio, and others, a number of solvents have been discovered with which it is possible to obtain perfectly limpid pseudo-solutions of rubber, which can be readily filtered, provided that one is content with low concentrations. Such are the ethereal and chloroform solutions.

Before methods were devised for the direct determination of rubber, it was always estimated by difference, after separating from its solution everything that was not rubber—that is to say, the resins, insoluble matter, acids, and mineral matter.

Under the obvious influence of Wallach's work, in connection with the employment of bromine, nitrosyl chloride, nitrous acid, phenylhydrazine, and hydroxylamine for the direct and accurate determination of the terpenes, all the efforts of analysts have been directed, in more recent times, towards the establishment of methods for causing rubber to enter into combination with various reagents, to form products which can be easily purified and sharply characterised, not only through their elementary chemical composition, but also by means of their physical constants, such as melting point, boiling point, density, and optical properties.

In the able hands, more particularly of Harries, Weber, Ditmar, Hübener, Hinrichsen, and Alexander, the result of this somewhat delicate work has not only been the foundation of sure and exact methods of analysis and specific determinations, but has also opened a way for the study of the constitution and structure of rubber, the secret of which has at length been revealed.

The coagulum obtained from latex contains, in addition to pure rubber, water; fragments of wood, or vegetable débris derived from the tissues of the producing tree; mineral matter made up of impurities contained in the serum, residual traces of the chemical coagulants employed, such as common salt, alum, organic or mineral acids; and, lastly, organic products other than pure rubber, such as insoluble oxidised rubber or nitrogen compounds.

It contains, further, protein substances, diastatic ferments, peroxidases, sugars of the inositol family and their ethers, such as *dambonite* (dimethyl ether), *matesite* and *bornesite* (methyl ethers), traces of terpenic compounds, and, finally, resins. Of the latter some are distantly related to rubber—viz., the inactive ethers of cinnamic acid ; others, which are not so well known, appear to belong to the cholesterol group ; they are quite unrelated to rubber, and are optically active.

We propose to consider in turn the isolation and analysis of each of these bodies, according to methods which have been established for a decade ; and, in doing so, we shall follow, in chronological order, the different investigations which have enabled the direct determination of rubber as well as the estimation of various impurities in the crude product to be carried out.

In an analytical investigation the sampling of the crude rubber is a matter of the very greatest importance, and it presents certain difficulties. Crude rubber, as its external appearance might lead one to suppose, is not a homogeneous product. The great variety of processes by which it is obtained affords a wonderfully good explanation of its heterogeneity. Henriques recommends the preparation of an average sample by cutting strips parallel to the faces and diagonals of the block to be analysed ; these are then cut up into thin fragments with a razor in a stream of water, and by thoroughly mixing these fragments together a homogeneous sample can be drawn representative of the whole block.

The determination of moisture is carried out either by drying a weighed sample in a vacuum desiccator over sulphuric acid, or, as suggested by Pontio, by heating a sample for two hours at 116° to 120° C. in a hot air oven, preferably in a current of carbon dioxide, to prevent oxidation.[1]

The determination of organic débris and mineral matter is effected by dissolving a known weight of the rubber in a large excess of benzene, and separating the insoluble matter by filtration ; the mineral matter is determined by incinerating the dried, weighed residue, and its constituents can be determined in the usual way.

In order to arrive at an accurate result, it is well to deduct, from the weight of the total insoluble matter, that of the insoluble rubber separated in a subsequent operation ; the difference is the weight of vegetable impurities plus mineral matter ; deducting from this the weight of the ash, the amount of vegetable impurities is obtained.

By washing with water the soluble impurities can be removed from the rubber ; these include the organic and mineral acids, soluble salts, and sugars, which can easily be characterised and estimated by the usual methods which need not here be detailed.

All raw rubbers, whether prepared by smoking or by chemical coagulation, contain acids, the whole of which may be extracted by macerating the rubber in hot or cold water for several days.

Clayton Beadle and Stevens obtained the following values, calculated as acetic acid, for the acidity of various rubbers :—[2]

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[1] According to Michelin, the moisture content of Para rubber, which was formerly about 14 per cent. on the average, tends to increase on account of the greater speed of transport, and to-day is as high as 18 to 20 per cent. Plantation rubber, washed and dried, does not contain more than 1 to 3 per cent.

[2] *Le Caoutchouc et la Guttapercha.*

ACIDITY OF VARIOUS RUBBERS.

Kind of Rubber.	Acetic Acid.
	Per cent.
Hard fine Para, A, ...	0·150
,, ,, B, ...	0·120
,, ,, C, ...	0·120
Soft ,, A, ...	0·132
,, ,, B, ...	0·168
Plantation Para, dark sheet, A, . . .	0·228
,, ,, ,, B, . . .	0·197
,, pale ,, A, . . .	0·292
,, ,, ,, B, . . .	0·240
,, ,, ,, C, . . .	0·150
,, ,, crêpe, A, . . .	0·120
,, ,, ,, B, . . .	0·017

It will be observed that the acidity of plantation Para, coagulated with acetic acid, and washed, is not much greater than that of wild Para, prepared by smoking and not washed. These experiments seem to show that the amount of acetic acid present in the smoke produced by burning green Itamba wood and palm nuts must be comparatively large, and it appears to be to the presence of this acid that the coagulation of rubber, in the smoking process, is mainly due.

The solvents of rubber are very numerous, and twenty years ago, as we have already mentioned, it was to them alone that recourse was had, in order to determine the amount of rubber in the crude product.

The latter was dissolved in the selected solvent, and the pure rubber was precipitated from the solution by means of acetone, or a mixture of alcohol and acetone, washed with hot alcohol, dried, and weighed.

The application of the new methods, based upon the formation of bromides, nitrosites, or ozonides, also demands the preliminary preparation of a solution, which is, moreover, necessary as a means of purification.

It will, therefore, be of value to consider these solvents, which are very numerous, and to see, first of all, by what laws their action is governed. The interesting observations made by Ditmar on this subject may be referred to.

Rubber, as a colloid, is not, strictly speaking, a soluble substance. It can only form pseudo-solutions and "swellings" (gonflements). Raelhmann points out that, when examined with the ultra-microscope, a colloidal solution appears, at first, as a mass of united particles, which can only be separated by diluting largely, and which in time grow smaller and disappear. They do not, however, dissolve, in the chemical sense of the word; they form what is called a *sol*. In spite of its apparent limpidity, if a beam of light be passed through such a solution, the continued existence of solid particles can easily be distinguished.

The first effect of solvents upon rubber is to swell up the "polyprene"; it then forms a network similar to a sponge or to a soap lather, in which dilute solutions are separated, by an osmotic membranous wall, from concentrated solutions or, better, *gels*.

The problem of solution, therefore, becomes a physico-chemical problem, based upon osmotic action, and it is this problem which Ditmar has studied. "The swelling of rubber," he says, "generally takes place more slowly than the passing into solution of a crystalloid; in studying the process, I proceeded in the following manner:—Purified Para rubber, reduced to exceedingly thin sheets and dried, was placed in a vessel, kept at 15° C., in contact with carbon disulphide, in the proportion of 1 grm. of rubber to 75 c.c. of solvent, in a mechanical shaker. A sample of the liquid was taken every ten minutes, placed in a tared glass vessel, evaporated, and dried to constant weight. In this way the progress of solution—or of diffusion—could be followed, and represented by a curve, in which times were plotted as abscissæ and percentages of rubber dissolved in carbon disulphide at 15° C. as ordinates."

It will be understood that such a method can be used for any solvent, and at any temperature. By its use solvent power, solution velocity, rate of swelling, and rate of diffusion (and thus the relative values of various liquids as solvents for rubber) can be accurately determined.

In the case of carbon disulphide, under the conditions stated, the swelling of the "polyprene" only begins after ten minutes' contact; after twenty minutes the curve rises steeply, and then flattens out.

The use of this method has led to the discovery that the presence of water in the rubber exercises a very great influence upon the rate at which it swells in solvents; treatment with hot water still further increases the speed of swelling. The simple explanation of this fact is that water swells the colloid superficially, and thus allows the disulphide to enter the rubber more rapidly.

It is the same with the resins: the higher the content of these, the more rapidly the rubber swells, to such a point that it appears to swell in the resins themselves. This fact has found a technical application in the Dybowski process for the treatment of resinous Borneo rubbers.

Ditmar correctly compares these two phases—diffusion and swelling—to the action of water on an anhydrous salt which is capable of yielding hydrated products, such as sodium carbonate, for example. In the first stage the substance absorbs water, giving rise to a crystalline product, and in the second stage it dissolves.

Under the microscope it is seen that, in the case of rubber, swelling goes on as long as there is any solid left; only when the whole of the rubber is swelled does diffusion begin to take place; the value of a solvent may, therefore, be denoted by stating the percentage quantity of rubber diffused in it in standard time.

Hoffer [1] maintains that in crude rubbers two distinct portions are present, the one capable of swelling, the other not, and on the relative proportions of these two depends the greater or lesser elasticity of a rubber.

Mastication alters these properties, and the swelling of the active portions acts, in the same way, upon the inactive parts; the cells of the non-swelling rubber are ruptured and modifications arise.

These results can be hastened, according to Hoffer, by using mixtures of solvents, such as carbon disulphide and alcohol, or benzene and eucalyptus oil, as proposed by Lascelles.

Ditmar has drawn up tables showing the amount of rubber diffusing into various solvents, in given times, and from these the relative value of the solvents can be judged. In each case 1 grm. of rubber per 100 grms. of solvent was used, and 180 shakes per minute were given to the vessel, which was kept at 15° C.

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[1] *Kautschuk und Gutta.*

THE VALUE OF RUBBER SOLVENTS.

Time in Minutes.	Rubber Diffused, per cent., in						
	CS_2. B.P. 47° C.	Benzene. B.P. 80° C.	Chloroform	Ether.	Toluene.	Carbon Tetrachloride.	Petroleum Benzine.
10	0·026	0·016	0·036	0·032	0·020	0·010	0·016
20	0·054	0·026	0·054	0·054	0·034	0·024	0·026
30	0·100	0·030	0·092	0·100	0·062	0·064	0·040
40	0·454	0·050	0·170	0·120	0·066	0·078	0·056
50	0·798	0·054	0·592	0·158	0·088	0·094	0·080
60	0·842	0·080	0·916	0·214	0·112	0·182	0·092
70	0·994	0·140	0·934	0·420	0·268	0·230	0·128

From these results carbon disulphide and chloroform would appear to be the best solvents of rubber.

The principal solvents of rubber are, in the first place, the products of the destructive distillation of rubber, such as caoutchene and heveene, or the complex mixture of hydrocarbons produced in the process; linseed and nut oils, the action of which was first pointed out by Fresneau in 1755; Dippel's oil, turpentine, camphor vapour, referred to by Hérissant and Macquer; hydrated ether—although open to discussion—benzene and its homologues, petroleum ether, carbon disulphide—the most active solvent—lavender oil, carbon tetrachloride, chlorine derivatives of ethane, boiling naphthalene (Kletzinsky), cymene (Pontio), nitrobenzene (Weber), petroleum spirit boiling above 150° C. (Henriques), chloroform, amyl acetate, dipentene, camphene, anthracene, creosote oil, pentane, rosin oils, sylvestrene, camphor oil, terpineol (Tixier), terpin oils and terpin, pinene hydrochloride (Dubosc), paraffin oil, anisole, phenetole, aniline, phenol (Casselmann), quinoline, benzaldehyde, pyridine, etc., etc.

Mixtures of two or more of these solvents are frequently employed, such as carbon disulphide and alcohol, petroleum benzine and benzene, turpentine and carbon tetrachloride, chloroform and nitrobenzene.

The boiling point of the solvent selected plays a considerable part in determining the rate of solution (in the hot). From this point of view excellent results are obtained with cumene, recommended by Pontio (boiling point, 150° to 160° C.).

In industrial practice, where it is not possible to use pure compounds, on account of their price, such solvents have to be chosen as have the best characterised boiling points. Thus amongst coal-tar naphthas Weber recommends the use of the fraction 75° to 140° C., Markwald and Frank the fraction 100° to 140°; in the case of shale oils, which are equally good solvents, Weber has recommended the portion passing over between 80° and 150° C. Carbon tetrachloride, upon which many hopes were built, on account of its non-inflammability and its great solvent power, has not in practice fulfilled anticipations. It is probable that this compound is possessed of great depolymerising power, and that the colloidal complex is broken down by it on passing into solution.

In a general sense, previous mastication or trituration greatly facilitates the solution of rubber, but a number of grave drawbacks are associated with the employment of these processes.

Boutaric's work, already referred to, has shown to what extent the physical constants are affected by mastication; it is obvious, therefore, that some deep-seated change must occur in the molecule under the influence of this process. By mastication, also, the amount of insoluble matter, which is often estimated by solution, is altered, becoming reduced progressively with the duration of the mastication process.

For this reason Beadle and Stevens employed petroleum benzine as solvent, and did not apply heat until after the complete swelling of the rubber, and then kept the temperature below 100° C. When the *sol* thus obtained was diluted with pure benzene the whole of the insoluble matter settled out, and a solution of rubber without, or with only a small amount of depolymerisation, was obtained.

The following table, drawn up by Fendler, shows the amount of various rubbers dissolving in three of the most usual solvents—viz., ether, benzene, and petroleum ether:—

SOLUBILITY OF RUBBER IN VARIOUS SOLVENTS.

Kind of Rubber.	Percentage of Rubber Dissolved in		
	Ether.	Petroleum Ether.	Benzene.
Crude Para,	46·0	33·0	63·0
Fine Para,	89·0	94·0	95·0
Washed Para,	97·0	96·0	96·4
Para Scrap,	75.5	80·95	93·2
Rio Janeiro,	85·0	93·3	92·0
Maniçoba,	95·0	95·0	92·0
West Indies Scrap,	95·8	96·8	95·4
Mexican Scrap,	85·5	89·5	88·2
Guatemala, Crude,	80·3	80·3	78·1
Madagascar,	87·9	92·5	92·5
Calabar,	64·8	55·3	68·0
Mozambique,	47·8	46·0	50·8
Cameroon,	96·0	94·8	93·7
Congo thimbles, red,	54·8	57·9	58·1
Isanguï,	80·0	81·8	79·2
Togo Manihot,	84·0	85·3	85·4
Bissao,	88·2	92·2	90·5
Ceylon Hevea,	72·9	86·9	96·7
Borneo, I.,	81·8	89·5	87·0
,, Ordinary,	69·8	94·6	92·0

All these solvents act both on the rubber and on the resins. In the case of benzene Fendler found the following proportions of each :—

SOLUBILITY OF RUBBER IN BENZENE.

Kind of Rubber.	Soluble in Benzene.		Insoluble.
	Rubber.	Resin.	
	Per cent.	Per cent.	Per cent.
Crude Para, ...	63·3	2·1	34·6
Washed Para, ...	95·4	2·7	1·1
Sernamby Para.	89·3	7·1	3·6
Crude Maniçoba, ...	92·0	6·3	1·7
West Indies Scrap, . . .	92·7	5·2	2·1
Mexican Scrap, ...	95·4	3·3	0·3
Guatemala, ...	88·2	11·7	0·1
Madagascar, ...	78·1	17·6	4·3
Calabar, ...	92·5	8·0	...
Cameroon, ...	93·7	4·6	1·7
Upper Congo, ...	89·7	4·8	5·5
Crude Mozambique, . . .	50·8	2·3	46·9
Purified Mozambique, . . .	89·8	6·2	4·0
Congo thimbles, ...	58·1	3·0	38·9
Togo Manihot, ...	85·4	6·2	8·4
Prime Borneo, ...	87·2	8·6	4·2
Ceylon Para, ...	96·7	2·1	1·2
Bissao, ...	90·5	4·8	4·7
Java, ...	92·0	5·2	2·8

The action of the various solvents differs a great deal. Some, like terpineol, nitrobenzene, xylene, and, in general, all those of high boiling point, act, according to Alexander's theory, both as depolymerising agents and as solvents ; the others cause the rubber to swell up, forming in the first place a *gel*, and later a *sol*. Rubber precipitated from solution in depolymerising solvents is viscous, or sticky, and only recovers its original properties with great difficulty.

Ahrens has published some very interesting work on the subject of rubber solutions,[1] and this may be quoted here on account of the valuable information which it contains. He remarks :—" It is customary to speak of raw rubber swollen by benzine, benzene, toluene, etc., as a rubber solution. All specialists know, however, that if what is called a colloidal solution be poured on to a filter it separates at once, and with the greatest ease, into its two constituents—viz., the colloid, and the solvent or swelling agent. There can be no question, then, of a true solution, in the proper sense of the word. It must, however, be recognised that, for example, a 1 per cent. solution of Para rubber can, under certain circumstances, be filtered, provided the raw rubber has been previously well worked at an elevated temperature."

Ahrens describes a method of preparing such solutions of Para rubber. The sample is cut into the smallest pieces possible, and is then heated in boiling water, and dried at 60° C. When dry, the pieces are placed, without kneading, in the swelling agent, benzine for instance, and left without dis-

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[1] *Chem. Zeit.*, 1910, 34, 266-267.

turbance until they have absorbed ten times their own weight of hydrocarbon, a process which takes several days. The mass is then gently shaken and heated on a water bath until it is completely dissolved.

It is always a great advantage to use amyl acetate, instead of benzine, for in that case the rubber dissolves completely, after eight days' digestion, forming a fluid solution which can be filtered through ordinary filter paper.[1]

The filtrate is of a fine amber colour, and about as mobile as castor oil. By adding a precipitant such as alcohol or acetone a white, very pure rubber is thrown out of solution; unfortunately this is readily oxidised in the air, and is easily decomposed by the action of light, or the ultra-violet rays of the mercury vapour lamp.

In preparing a highly purified rubber for purposes of research the use of a depolymerising solvent—such as turpentine or terpineol—must be carefully avoided, since these of necessity affect the physical constitution and structure of the rubber. Chloroform and carbon disulphide appear to be particularly suitable for this purpose.

Often, following the example of Hinrichsen or Harries,[2] a preliminary solution of the rubber in petroleum-benzine, camphor oil, or toluene is made, and the rubber is then precipitated by alcohol and redissolved in anhydrous benzene or chloroform, the latter process being repeated several times.

When purified Para rubber is treated with ether, 66 to 68 per cent. of it dissolves, leaving behind 34 to 32 per cent. of a brown, insoluble substance. Turpentine, under the same conditions, leaves 50 per cent. of coloured matter undissolved. The power of different solvents varies markedly. Thus the heavy coal-tar oils dissolve only 5 per cent. of their own weight of rubber, whilst the lighter oils give *sols* containing 30 per cent. of rubber.

The best solvent appears to be carbon disulphide containing 5 per cent. of alcohol.

The following "solubilities" have been recorded for various types of lower-grade rubbers:—

SOLUBILITIES OF LOWER GRADE RUBBERS.

SOLVENT. 100 Parts.	RUBBER.		
	Ceara.	Negroheads.	Sierra Leone.
	Per cent.	Per cent.	Per cent.
Ethyl ether, ...	2·6	3·6	4·6
Turpentine, ...	4·5	5·0	4·6
Chloroform, ...	3·0	3·7	3·0
Petroleum benzine, . . .	4·4	5·0	4·7
Carbon disulphide, . . .	0·4	...	...

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[1] In using a filter pump, Pontio obtained good results with moulded pump plates of China clay and cellulose, and also with the paper used for printing copper-plate engravings.

[2] *Monit. Scient.*, 1904, 18, 201.

The production of thick varnishes is comparatively easy. Heeren gives the following table for their preparation with benzene and various rubbers :—

RUBBER VARNISH.

Kind of Rubber.	Dissolved in 100 Parts of Benzene.
Guayule,	25·0
Para,	20·0
Carthagena,	18·0
Borneo,	15·0
African,	14·5
Ceara,	13·6
Mozambique,	13·0
Quisambo,	10·0
Rangoon,	9·8
Knikels,	9·4
Niggers,	8·5
Madagascar,	6·0

These variations in solubility are very curious, and no very precise explanation has been given of them.

Some, supporting the theory which assumes that two isomeric hydrocarbons, with different mechanical properties, are present in rubber, maintain that only the plastic portion dissolves, or at least forms a colloidal solution, or *sol*, whilst the more elastic part simply swells up enormously forming a *micella*.

Harries does not appear to share this view, for he finds that rubber, freshly precipitated by alcohol from a solution, is always soluble in ether. It loses this property on heating, but recovers it on boiling with glacial acetic acid. Ethereal solutions, prepared in this way, are useful in experiments on reduction by hydrogen in presence of colloidal palladium, by Paal and Skita's method, experiments which hitherto have not succeeded in the case of rubber.

In addition to the two forms of precipitated rubber referred to above, which are both soluble, Harries has obtained a third, oily form. He prepares it by heating any rubber solution, and then precipitating with alcohol. In this form, which, unfortunately, is often obtained in reclaiming processes, the rubber is much more soluble than the coagulated form.

It may be that this oil is allied to the body isolated by Weber from *Castilloa*. We have noticed that, on adding freshly precipitated, non-oily rubber to it, it is gradually transformed into a solid coagulate.

An almost similar result is obtained with hydrogen chloride at low temperatures, but the coagulate then becomes quite insoluble, and must be boiled with acetic acid to render it soluble.

Marcusson and Hinrichsen, who have devoted much study to the rubber resins, defined them as " substances soluble in acetone and alcohol found in the crude product obtained from latex." The impurities represent a fairly important content, and the first series of researches of which they formed the subject was carried out by Terry in 1892 ; Weber took up their study in 1895 and Spence in 1906. The following figures have been given by various authors :—

RESIN CONTENT OF RUBBER (*Various Authors*).

Kind of Rubber.	Resin Content.		Melting Point of Resins.
	Terry.	Weber.[1]	Terry.
	Per cent.	Per cent.	° C.
Para, ...	1·2	1·3	5
Ceara, ...	1·3	2·1	2
Columbian, ...	2·5	3·8	...
Mozambique, ...	3·0	3·2	18
Rio Janeiro, ...	5·8	5·2	64
Madagascar, ...	6·1	8·2	...
Sierra Leone, ...	7·4	9·7	...
Borneo, ...	7·9	11·7	28
Assam, ...	9·3	11·3	82
Mangabeira, ...	10·5	13·1	48
African Ball, No. 1, . . .	18·5	22·8	38
,, ,, 2, . . .	22·8	26·1	20
,, ...	41·2	63·9	20

RESIN CONTENT OF RUBBER (*Spence*).

Source of Rubber.	Resins.	Source of Rubber.	Resins.
	Per cent.		Per cent.
Hevea Braziliensis (1), .	2·73	Ficus elastica, . .	6·81
,, (2), .	3·93	Funtumia elastica (1), .	10·56
Funtumia (1), . .	19·72	Landolphia thalonii (1),	3·34
,, (2), . .	17·71	,, ,, (2),	7·02
Hevea Braziliensis (3), .	2·31	Funtumia elastica (2), .	5·54
Funtumia (3), . .	4·12	Landolphia, . . .	4·97
Ficus Vogelii, . .	35·37	Hancornia speciosa, .	4·35

Terry's figures were obtained by extracting the rubber, cut up into small pieces, in a Soxhlet apparatus with absolute alcohol; Weber dissolved in benzene and precipitated the rubber by the addition of alcohol.

The melting points given by Terry are of only secondary importance, for the resins are themselves mixtures of different compounds, which it would be necessary to separate and examine individually in order to obtain a useful result. Work in this direction has been done by Tschirch and Muller, Cohen, Alexander, and others.

Fendler has also made determinations of the resin in various rubbers, and his results are given below :—

RESIN CONTENT OF RUBBER (*Fendler*).

Kind of Rubber.	Resins.	Kind of Rubber.	Resins.
	Per cent.		Per cent.
Para, ...	2·1	Sapium, ...	7·1
Amazonian Euphorbia,	4·5	Upper Guinea, . .	20·6
Upper Congo, . .	4·8	Borneo, ...	24·47
German East African, .	4·9	Pontianak, ...	72·0
Java, ...	5·2	Jelutong (dry), . .	81·0

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[1] *Chem. Zeit.*, 1894, 18, 1903.

It will be seen that the figures obtained by different analysts are in close agreement, and that the resin content varies, roughly, inversely as the commercial value of the different kinds of rubber. Brazilian rubbers and those of Ceylon and Java are pretty pure in this regard, whereas Central Africans and the resinous rubbers of the Straits Settlements have such a high resin content that their study as rubbers becomes of little interest.

The work of Tschirch, Bourne, and Spence, following on that of Terry, Weber, and Fendler, is limited to the determination of the amount of resins contained in various rubbers, and the description of their appearance, melting points, and some of their reactions. In very rare instances they have attempted to establish the chemical formulæ, or to determine the molecular weight of certain compounds isolated from these resins.

The end in view in these researches has been more particularly to establish the percentage of impurities present in rubbers from various sources, since the value of these will be greater the smaller the amount of these foreign bodies present.

Other methods of investigation have been worked out in connection with this subject.

Harries established the fact that the fundamental hydrocarbon of rubber has a symmetrical constitution; hence it is devoid of optical activity. On the other hand, some of the rubber resins are optically active, and can, after extraction by acetone, therefore, be examined by means of the polarimeter and classified.

The following is a summary of the results obtained by Kindscher and Manasse, who have given attention to this branch of investigation:—

OPTICAL PROPERTIES OF RESIN FROM RUBBER.

RESINS FROM	Observed Rotation.	Specific Rotation. $[\alpha]_D$
Hevea Rubber, ...	Inactive.	Inactive.
Manaos Rubber, ...	+0·06°	+12·5°
,, ,, ...	+0 06°	+16·2°
Upper Congo Rubber, .	+0·12°	+12·5°
Peruvian, ...	+0 23°	+29·5°
Dead Borneo, ...	+5·02°	+49·4°
Padang Rubber, . . .	+0·35°	+28·0°
Guayule Rubber (α), . . .	+0·59°	+13·8°
,, ,, (β), . . .	+0·34°	+15·5°
Kassai, ...	+0·55°	+29·1°
Kickxia, ...	+0·08°	+32·9°

In these experiments the resins were extracted with acetone, the solvent evaporated, and the residue taken up in benzene. In cases where these solutions were too highly coloured, the colour was reduced either by dilution, or by heating the solution with Fuller's earth.

It was found, as the above table shows, that Hevea rubbers, whether obtained from Ceylon or from the Amazon, contain resins which are optically inactive; it is more than likely that they contain no resins related to cholesterol. Hence the employment of optical methods, under the conditions described, enables these rubbers, which are regarded commercially as the best grades, to be distinguished from all others. Kindscher and Kuster, in carrying this work to completion, investigated the amount of saponifiable constituents present in these resins. The acetone extract was evaporated to dryness and the residue heated for half-an-hour with $\frac{N}{2}$ alcoholic potash; the unsaponified constituents were taken up in light benzine equal in volume to the alcoholic potash used, according to the method of Spitz and Honig.

The resin acids were precipitated from the alkaline extract and examined separately. The proportion of unsaponifiables in the resins from various rubbers was found to be as follows:—

Rubber.	Unsaponifiables in Resins.	Rubber.	Unsaponifiables in Resins.
	Per cent.		Per cent.
Dead Borneo, . .	100·0	Kickxia, . . .	74·0
Kassai, . . .	92·6	Congo, . . .	56·6
Padang, . . .	90·2	Ceylon, . . .	20·8
Guayule, . . .	78·2	Para, ...	15·0

Notable differences in the solubility of the resins in alcoholic potash are apparent from the above figures, which, according to Spitz and Honig,[1] are complementary to determinations of optical activity. From the following tabulated figures it is evident that the optical activity resides in the unsaponifiable portion of the resins mainly or entirely, the portions soluble in alkali showing little or none; the inactivity of the Hevea resins is in accord with their low percentage of unsaponifiable constituents.

OPTICAL PROPERTIES OF UNSAPONIFIABLE RESINS.

Kind of Rubber.	Rotation of Unsaponifiable Resins.		Specific Rotation of Original Resin. $[\alpha]_D$.
	Observed.	Specific. $[\alpha]_D$.	
Hevea—Ceylon or Para, . .	Inactive.	Inactive.	Inactive.
Dead Borneo, ...	+0·25°	+49·6°	+49·6°
Kassai, ...	+0·40°	+34·4°	+29·8°
Padang, ...	+0·31°	+40.2°	+29·4°
Guayule (α).	+0·22°	+27·9°	+12·5°
,, (β), ...	+0·28°	+28·5°	+15·2°
Kickxia, ...	+0·22°	+27·0°	+32·0°
Congo, ...	+0·24°	+24·5°	+13·0°

These observations were afterwards supplemented by others dealing with a much larger number of types, which are summarised in the following tables:—

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[1] Holde, *Minerale Öle und Fette*, 1905.

RUBBER.	Observed Rotation.	Specific Rotation. $[\alpha]_D$.	RUBBER.	Observed Rotation.	Specific Rotation. $[\alpha]_D$,
Aruwimi,	+2·59°	+31·2°	Mattagrosso,	+0·74″	+46·4°
Cameta,	+1·85°	+36·6°	Para,	Inactive.	Inactive.
Caucho ball,	Inactive.	Inactive.	Cameta,	+0·26°	+18·0°
Gambia,	+0·37°	+16·55°	Kassai,	+0·32°	+13·7°
Guayule,	+0·15°	+11·7°	Congo black,	+0·85°	+33·7°
Java,	+6·62°	+62·9°	Manaos negroheads,	+0·08°	+13·5°
Congo,	+1·77°	+25·8°	Maniçoba,	+1·8°	+42·8°
Loanda,	+1·02°	+22·2°	Massai niggers,	+0·49°	+16·3°
Madagascar,	+8·15°	−35·3°	Mattagrosso,	Inactive.	Inactive.
Manaos,	+0·18°	+23·0°	Peruvian ball,	+1·25°	+ 38·9°
Maniçoba,	+0·38°	+27·5°	Thimbles,	+0·55°	+22·1°
Massai,	+0·64°	+21·0°			

On saponification the following figures were obtained :—

RUBBER.	Unsaponifiable Resins.	RUBBER.	Unsaponifiable Resins
	Per cent.		Per cent.
Aruwimi,	99·5	Maniçoba,	79
Gambia,	87	Massai,	83
Guayule,	57	Mattagrosso,	95
Java,	98	Para,	56
Loanda,	98	Pontianak,	77
Manaos,	72	Mattagrosso,	78

and the comparison between the rotation of the original resins and that of the unsaponifiable portion is shown by the following figures :—

RUBBER.	SPECIFIC ROTATION OF		RUBBER.	SPECIFIC ROTATION OF	
	Unsaponifiable.	Original Resins.		Unsaponifiable.	Original Resins.
Aruwimi,	31·6°	31·3°	Mattagrosso,	53·5°	46·4°
Cameta,	37·2°	36·9°	Pontianak,	57·2°	49·6°
Gambia,	13·7°	12·6°	Cameta negroheads,	35·5°	18·0°
Guayule,	15·4°	11·7°	Kassai,	15·0°	15·2°
Java,	62·2°	63·2°	Congo black,	30·3°	33·7°
Congo,	24·4°	25·7°	Manaos negroheads,	24·0°	13·5°
Loanda,	23·6°	22·2°	Maniçoba,	47·5°	42·8°
Madagascar,	39·9°	35·6°	Massai niggers,	17·1°	13·5°
Manaos,	27·7°	23·0°	Peruvian ball,	42·7°	38·9°
Maniçoba,	Inactive.	27·5°	Thimbles,	25·1°	23·7°
Massai,	21·0°	20·0°			

As in the first series, the activity of the unsaponifiable portion is greater than that of the original resins, except in the case of Maniçoba, where the unsaponifiable constituents are inactive. Since the saponifiable portion is also totally inactive, it must be assumed that racemisation occurs under the influence of the alcoholic soda. Some of these impurities have been examined chemically, and it will be of interest to reproduce the results of these investigations, which complete the information at our disposal with regard to the rubber resins.

Pontianak resin, which constitutes about 80 per cent. of the ordinary gum, was examined by Weber,[1] who separated from it its principal constituent, a substance melting at 161° C., to which he gives the formula $C_9H_{12}O$, based on the following analytical results :—$C = 78 \cdot 18$; $H = 9 \cdot 19$; $O = 12 \cdot 63$ per cent.

Different results were obtained by Alexander, whose analytical figures for the substance melting at 161° C. were :—$C = 84 \cdot 25$; $H = 11 \cdot 41$; $O = 4 \cdot 34$ per cent. From these he deduced the formula $(C_{10}H_{16})_5O_2$.

Tschirch and Müller[2] have given identical figures for a resin separated from Mozambique balls. These substances would appear to be oxidation products of rubber and not true resins; their molecular weight is 712. Hinrichsen and Marcusson are not of this opinion, believing it to be more reasonable to suppose that the substance is an alcohol of the cholesterol series, such as phytosterol. Our own experiments lead us to the same conclusion. One must, indeed, expect to meet with products of this kind in vegetable juices.

In *Euphorbia* rubber Cohen[3] found 7 per cent. of resins ; the alcoholic extract contains β-amyrine acetate, and a derivative of phytosterol of the composition $C_{30}H_{30}O$, $2H_2O$; this does not yield lupeol on saponification, but a phytosterol $C_{22}H_{40}O$, H_2O, closely allied to the *iso*cholesterol of wool fat ; it crystallises in needles from acetone. Its benzoate also crystallises in needles, which melt at 193° C. ; its acetate crystallises in leaflets melting at 134°.

In Pontianak resin, Sack and Tollens found an alcohol-, alstol-, and two other compounds, alstonine and *iso*alstonine.

From Mozambique balls, Tschirch and Müller separated a resin having the formula $C_6H_{12}O$ and melting at 178° C.

In Congo rubber a resin is present which has the composition : $C = 70 \cdot 9$; $H = 10 \cdot 8$; $O = 18 \cdot 3$ per cent., and melts at 271° C.

In the resins extracted from Jelutong[4] we have found two different substances, characterised by their solubilities in alcohols and ethers, and having melting points varying from 85° to 118° C.

These resins behave differently towards concentrated sulphuric acid, one of them giving a red colouration with a very marked green fluorescence, the other acquiring a brown tint which rapidly changes to black. Both are soluble in fuming nitric acid, but whereas the addition of water to one of these solutions brings about a copious yellow precipitation, no precipitate is produced with the other. All the resinous Borneo rubbers appear to contain resins similar in character to those examined by us.

Besides alcohol and acetone, which are generally employed to dissolve rubber resins, Wagner found that the following solvents were available :—Ether, benzene, petroleum ether, carbon tetrachloride, carbon disulphide, acetic acid, dichlorhydrin, and nitrobenzene. He also noted, as we did, that on contact with concentrated sulphuric acid a red colouration with a green fluorescence was produced, and that yellow flakes were precipitated from a solution of the resins in fuming nitric acid, on dilution with water.

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[1] *Gummi Zeit.*, 1903.

[2] *Gummi Zeit.*, 1904, 19, 867.

[3] *Die Harze.*

[4] Dubosc, "Analyse des Résines du Djelutong," *Le Caout. et la Guttapercha*, 1911.

Robinson, Dreyfus, and Bentley determined their solubility in pyridine, and other bases of the pyridine group, and Hanriot suggested as the best solvent a mixture of four volumes of petroleum ether and three volumes of acetone. One litre of this mixture dissolves about 250 grms. of resin at 23° C.

Oehler's determinations of the iodine values of various rubber resins, by Hübl and Kaller's method, gave the following results:—

IODINE VALUES OF RUBBER RESINS.

Rubber.	Iodine Value of Resins.
Dead Borneo,	30·6
Para,	118·0
Padang,	87·1
Kassai,	107·0
Guayule,	94·1

There is no regularity about these figures, and it is not possible to draw definite conclusions from them. Generally speaking, high iodine values merely indicate the presence of unsaturated hydrocarbons. Otto Kornek maintained that the resins yielded a solid ozonide, on treatment with ozone, and that this ozonide was insoluble in carbon tetrachloride, but his results have been disputed, and the method suggested by him does not appear to be applicable to the determination of rubber. Ditmar and Wagner have shown, on the other hand, that the resins will combine with sulphur; the product is a very brittle mass, and its presence in vulcanised rubber greatly reduces the strength and elasticity of the latter.

Lastly, besides the optical methods which we have summarised, Wagner put forward the following method of analysis:—To determine the resins, a given weight of raw rubber is dissolved in a litre of pure benzene, and the solution is filtered through silk gauze; 100 grms. of the filtrate is then poured drop by drop into 200 grms. of alcohol (95 %), and the rubber which separates is filtered off and washed with hot alcohol. The filtrate and washings containing the resins are evaporated to dryness in a tared flask and weighed.

Employing this method for their isolation, Wagner studied a number of rubber resins. He found that the resin of Congo rubber is soluble in alcohol, ether, acetone, benzene, chloroform, petroleum ether, carbon tetrachloride, carbon disulphide, ethyl acetate, dichlorhydrin, nitrobenzene, and acetic acid. The colour of the solutions varies from yellow to brown. The resin dissolves in sulphuric acid, forming a cherry-red solution with a green fluorescence; and in fuming nitric acid giving a yellow or brown solution from which yellow flakes are precipitated on the addition of water.

The resin is also soluble in acetic anhydride when heated, forming a yellow solution, which becomes turbid on cooling; on adding a drop of sulphuric acid (Liebermann's cholesterol reaction) a red colouration is produced, changing to a dirty brown and then to green. After standing for a long time the liquid becomes coffee-coloured, and ultimately brownish-violet. On heating, it becomes brownish-red, and finally onion-coloured. On shaking a solution of the resin in chloroform with a little sulphuric acid (Hesse and Salkowski's cholesterol reaction), the chloroform layer becomes at first brownish-yellow, then, after several hours, faintly violet, with a green fluorescence. The resin of Madagascar rubber gives the same reactions, but it is less soluble in alcohol. Its solution in acetic acid becomes reddish onion colour on the addition of sulphuric acid, then changes at once to a dirty brown.

Borneo resin gives practically the same reactions, but contains a constituent which is insoluble in several solvents. Solutions in alcohol, carbon disulphide, and petroleum ether are cloudy; in the course of our own investigations we have made the same observations on this point as Wagner. Dichlorhydrin dissolves this resin on heating, giving a brown solution.

In Tschirch's reaction the chloroform-sulphuric acid surface does not become coloured more rapidly than the rest of the chloroform layer. From the solution of Congo resin in sulphuric acid brilliant crystals, consisting of rectangular plates, separate after a few days.

The resins extracted from the majority of these rubbers appear to be closely related to cholesterol, and to be secondary alcohols capable of esterification by means of organic acids.

From this information it will be seen that the resins can be fairly easily determined, either by Wagner's method, or by the optical method and saponification. In this respect, therefore, it is a simple matter to find out the degree of purity of a natural rubber.

Alexander,[1] who has handled very considerable quantities of the Guayule shrub in the course of industrial treatment of the plant for the production of rubber, has studied the resins present very closely.

Guayule, as it comes on to the market, contains from 12 to 25 per cent. of matter extractable by acetone. In continuous treatment on an industrial scale, Alexander obtained a greenish-black extract, of the consistency of honey, from which colourless crystals separated on standing. Of the extract, 54 per cent. is soluble in petroleum ether, 31 per cent. in ether, and 15 per cent. in alcohol.

These greenish-black solutions contain chlorophyll; the residue from the petroleum ether extract is soft, whilst that from the other extract is hard. The first contains 12 per cent. of saponifiable matter, the second 7 per cent., and the third 2 per cent. In addition to these products, Alexander succeeded in isolating an acid melting at 119° C., which crystallises from water, and, like other acids separated from these extracts, is very susceptible to chemical change, and cannot be obtained in a sufficiently pure state. It appears to belong to the cinnamic acid series.

This acid has been isolated more easily and in fairly large quantity from the acetone extract of Guayule prepared by the alkali method. After being twice crystallised from ether, it had a melting point of 79° C., and gave on analysis: $C = 69{\cdot}47, 69{\cdot}74$; $H = 6{\cdot}80, 6{\cdot}75$; calculated, 70, 59; 5·89.

Alexander thinks it may be regarded as a phenylacetic acid

The composition of Guayule resin is thus quite different from that of other rubber resins, its solubility in various liquids, its saponification value, the presence in it of an acid such as phenylacetic acid, constituting it a substance quite apart, and one which demands exhaustive study.

Whereas both rubber itself and the rubber resins can, under certain conditions, be dissolved in selected solvents, there are certain other bodies present in raw rubber which resist the action of all solvents. These are what

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[1] Rubber Lectures, London, 1911.

are called the *insoluble constituents* of rubber, products about which much discussion has been, and is still, carried on.

Some have looked upon them as oxygen derivatives of rubber, either natural or formed by the action of atmospheric oxygen on the rubber. Others have regarded them either as made up of the proteins derived from the latex, or of the enzymes or co-ferments by which the formation of rubber has been brought about; others again regard them as rubber in a state of super-polymerisation. It is probable that there is some truth in each of these divergent opinions, and that the insoluble constituents are made up of oxidised rubber, nitrogen compounds, and super-polymerised rubber.

Weber, in a masterly study published in 1900,[1] has gone into the question very thoroughly. He says:—" If crude rubber be treated with chloroform or carbon disulphide, it gradually dissolves, separating into two parts, one soluble, the other insoluble, and showing under the microscope a peculiar reticular structure, to which attention was drawn by Payen." The content of insoluble matter is subject to great variations; Ladenburg says that it varies from 30 to 70 per cent.; Gladstone and Hibbert found only 4 per cent. in Para rubber; Wiesner and Fendler have found it in other kinds of rubber without determining the amount; Burghard estimates it at 20 per cent.

Gladstone and Hibbert thought that the substance was formed during the smoking process, basing their opinion upon the observation that if the *soluble* fraction be heated it is partially converted into an insoluble [2] form. Seeligman regards it as a compound isomeric with rubber.

Weber isolated the insoluble constituent in the following way:—The rubber was freed from moisture and resins by repeated maceration in acetone, and was then, after drying, put to soak in chloroform. In the course of a fortnight a solution was obtained which separated into two layers; the lower layer was clear and limpid, and the upper one cloudy with wisps of insoluble substance, which had more or less retained the form of the original pieces of rubber. This layer was decanted, and washed repeatedly with chloroform, until no more soluble material could be extracted from it.

Dealing with Para, the amount of insoluble matter separated in this way was 6·5 per cent. of the rubber taken. The substance swells enormously in solvents, but in that condition has no adhesive properties; when dry it is supple, but only slightly extensible.

On analysis, the following figures were obtained:—$C = 61{\cdot}13$; $H = 10{\cdot}85$ per cent. $C_{30}H_{64}O_{10}$ requires $C = 61{\cdot}64$; $H = 10{\cdot}95$ per cent.

This result shows how erroneous is the view that this substance is an isomeride of soluble caoutchouc; it is quite a different thing, and is remarkable for its high hydrogen content, and the high proportion of oxygen—28·02 per cent. by difference.

In earlier work, such as that of Spiller,[3] the presence in rubber of a substance containing oxygen had been demonstrated, and the analytical results obtained with this compound are found to agree with the formula $C_{30}H_{58}O_{10}$. It appears to be a terpene derivative. The insoluble substance found by Weber in Para has the formula $C_{30}H_{64}O_{14}$, and the excess of hydrogen seems

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[1] " On the Nature of Rubber," *J. Soc. Chem. Ind.*, 1900, 19, 215.

[2] The explanation of this phenomenon has been given by Harries. The rubber which has been rendered insoluble by heat again becomes soluble after heating with boiling acetic acid.

[3] *Trans. Chem. Soc.*, 1865, 18, 44.

to indicate that it is not derived from the same hydrocarbon as Spiller's compound. The latter appears to be an additive compound of oxygen and rubber, whereas Weber regarded the insoluble constituent of Para as a hydrate of "polyprene"—$C_{30}H_{48}$, $10H_2O$—this formula being in as good agreement with the analytical values as $C_{30}H_{64}O_{14}$. On this Weber framed a bold hypothesis, to which we have already referred in dealing with the formation of rubber in rubber plants.

He would regard the insoluble constituent, not as the result of a hydrolytic transformation of rubber, but rather as an intermediate compound in the process of transformation of vegetable carbohydrates, of the cellulose type, into rubber.

Unfortunately, Weber states that he was only able to discover this substance in Para rubber, having searched for it in vain in Congo, Borneo, Assam, and Lagos rubbers.

On analysis, the soluble portion of rubber is found, after repeated purification, to have the following composition :—$C = 87·91$; $H = 11·86$ per cent. $C_{10}H_{16}$ requires $C = 88·23$; $H = 11·76$ per cent. It contains, therefore, about 0·4 per cent. of oxygen. In what form is this present in this soluble portion ? Is it derived from the insoluble constituent with which the soluble portion may be still contaminated ? Is it an additive compound or other oxidation product ? On account of the great difficulty of separating a mixture of colloids into its components one can only offer, in answer to these queries, Weber's hypothesis. His view was that the combustion of a large number of samples, all purified by means of acetone, has given figures which differ in different samples. These deviate more or less from the theoretical values for the formula $C_{10}H_{16}$, but in such a way as to leave no doubt that all these samples of rubber, whatever their origin, have the same empirical formula as the terpenes, though containing a percentage of oxygen, which is usually low, and varies, not only as between rubbers from different sources, but also as between two samples of the same kind of rubber.

The following are results of elementary analyses :—

KIND OF RUBBER.	Carbon.	Hydrogen.	Oxygen.	Ratio. C : H
	Per cent.	Per cent.	Per cent.	
Para, ...	87·87	11·51	0·61	10 : 15·7
Congo ball, . . .	85·15	10·82	4·02	15·2
,, . . .	86·41	11·07	2·51	15·3
Borneo, ...	86·63	10·83	2·53	15·0
,, ...	87·76	11·23	1·00	15·3
Ceara, ...	83·21	11·41	5·37	16·4
,, ...	86·20	11·56	2·23	16·0
Lagos, ...	86·11	11·54	2·34	16·0
Sierra Leone, . . .	86·38	11·34	2·27	15·7
Assam, ...	87·17	11·47	1·35	15·8
Mangabeira, . . .	87·08	11·39	1·52	15·7

These results show, as far as the evidence goes, that all these varieties of rubber consist essentially of the same hydrocarbon, $C_{10}H_{16}$, that their oxygen content may vary within fairly wide limits, but that it does not affect the terpenic ratio of carbon to hydrogen. But this can only be the case if the impurities present are addition compounds of oxygen and $C_{10}H_{16}$. Moreover, such an oxidation of rubber is of very frequent occurrence, and Weber himself obtained, by treating purified rubber with ethereal hydrogen peroxide, compounds similar to those which form the subject of the analyses just quoted.[1] According to Brindejonc, the formation of these oxidation products is much facilitated by light and heat, and by weak acids.

Kuster quotes a striking example of the oxidation of pure rubber.[2] Rubber was separated from a latex which had been previously heated, and was then freed from resins by extraction with acetone; the resin content amounted to 5·22 per cent., with a specific rotation of 32° 9′. The deresinified rubber was then left exposed to the air and light for a month. At the end of this time the white mass, which was scarcely tacky to begin with, had been converted into a brown, very adhesive substance, which, on extraction with acetone, yielded 3·11 per cent. of an optically inactive oxidation product.

According to Ahrens, the processes of washing and sheeting facilitate oxidation, which also takes place with special rapidity when rubber swollen with solvent, or solutions of rubber in benzene or chloroform are exposed to light.

Under the influence of ultra-violet radiation, on the other hand, oxidation is much more rapid than with ordinary sunlight. This is not surprising in view of what is known to-day of the effect of the ultra-violet rays in facilitating chemical combination. To sum up, it would appear to follow from the observations referred to that rubber contains two kinds of insoluble constituent, one which appears to be the remains of an intermediate substance in the formation of the rubber, and the other an addition compound formed by oxidation.

Spence has found a third constituent present in the insoluble portion; this contains nitrogen, and seems to be made up of proteins and enzymes derived from the latex. Spence says[3] that it has been known for a long time that the latex of all rubber plants contains substances analogous to the animal and vegetable proteins. These substances behave as proteins, and remain in the rubber on coagulation. Chemical examination has established the presence of protein in the latex, and its presence, in the coagulated form, in crude rubber has been inferred from the presence of insoluble nitrogen in technically pure samples of washed rubber.

The decomposition and putrefaction which occur in certain moist rubbers are due to the presence of these proteins.

Spence, somewhat after the manner of Weber, exhaustively extracted a sample of rubber with chloroform, and then conducted an elementary analysis of it, determining the nitrogen present, which Weber had neglected to do.

The amount of insoluble matter found was 2 per cent. The amount of nitrogen in the residue was rather variable; in five analyses the following results were obtained :—N = 1·9, 2·5, 2·5, 3·5, and 4·2 per cent., the highest result being obtained with a rubber which had been subjected to the extraction process for three months.

From these data the percentage of protein present may be deduced. On the most favourable assumption the lowest percentage of nitrogen corre-

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[1] *Zeit. anal. Chem.*, 1885, 24, 7, 25.

[2] Oxidation of rubber in the air goes on constantly, as shown by Herbst and Weil; one of these authors found in the product organic acids, the other levulinic aldehyde, which is also formed by the action of ozone.

[3] *Quarterly Journal*, 1907, v. iii.

sponds with a protein content of 10·87 per cent. in the insoluble matter, and the highest percentage with 33 per cent. of protein. It seems quite evident that, in addition to Spence's protein, the insoluble constituent must contain some other substance, and that that can only be the product indicated by Weber, or the super-polymerised rubber which Fendler believes to be insoluble in the usual solvents.[1]

The residue, according to Spence, gives the xanthoproteic reaction with strong nitric acid, but this is not an indisputable proof of its protein character, since pure rubber itself also gives this reaction under the same conditions.

The last traces of impurity—rubber or its oxidation products—cannot be separated from the nitrogenous constituents. Spence employed the microscope to differentiate between them.

In the voluminous jelly, obtained with Para rubber, thread-like structures are seen to be distributed through the whole mass; since sections are not stained by organic colouring matters, no structure is apparent in a section. But when heated with silver nitrate and tannin they present, under the microscope, an appearance strongly reminiscent of that of the fibrin in coagulated blood.

The rubber with which Spence worked having been freed from its resins, the above effect cannot be attributed to the reducing action of the latter, and it must, therefore, be due to the nitrogenous substance.

In order to explain the excessive swelling of the insoluble constituent with solvents, Spence supposes that the thin filaments of nitrogenous substance enclose rubber, and that whilst chloroform is able to penetrate the nitrogenous membrane and swell the rubber within, the dissolved rubber cannot pass outwards. Vigorous shaking, or mastication, destroys this state of affairs, by breaking up the nitrogenous envelope.

When dealing with the analysis of latex, we described Spence's experiments in connection with the oxidising enzymes present in it. This English chemist has carried out similar work with coagulated rubber.[2] In some forty samples examined, these enzymes are present in the insoluble substance, and it is to them that the discolouration which so rapidly takes place in rubber after its coagulation is due.

The changes of colour which are observed in freshly cut vegetable tissues have generally been attributed to the action of oxidases; this view is shared by Sapek, Weber, Tschirch, Schidrowitz, and Kaye.

Spence attempted to isolate these enzymes, in the following way:—A large quantity of rubber, cut up into small pieces, was soaked in water for seven or eight days; the aqueous extract obtained rapidly gave a deep blue colouration with tincture of guaiacum in presence of hydrogen peroxide, a reaction characteristic of peroxidases. The extract was alkaline to litmus, and, when treated with Millon's reagent, appeared to give distinct indications of the presence of protein. After dialysis it gave all the indications of an indirect oxidase, which is inactive save in the presence of hydrogen peroxide. The reactions of the extract after boiling, and with and without hydrogen peroxide, are summarised in the following table:—

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[1] *Gummi Zeit.*, 1904, 19, 43.

[2] *Le Caout. et la Guttapercha*, 1908, 5, 2029.

REAGENTS.	TIME.		
	10 Minutes.	1 Hour.	5 Hours.
	10 c.c. Extract + H_2O_2.	10 c.c. Extract only.	10 c.c. Extract + H_2O_2.
Tincture of Guaiacum,	Pure white,	Pure white,	Deep blue.
p-Phenylene-diamine,	Nil,	Nil,	,, brown-red.
o- ,, ,,	Pale yellow,	,,	Yellow, then red.
a-Naphthol,	Nil,	Distinct brown,	Distinct brown.
Phenolphthalein,	Pale pink,	,,	Deep pink.
Hydroquinone,	Nil,	,,	Bright red.
Amidol,	Pale pink,	Pale pink,	Deep cherry red.
Pyrogallol,	Nil,	Nil,	Yellow, brown deposit.
Indophenol,	Pink,	,,	Deep violet.
Tyrosin,	Nil,	,,	Nil.

These experiments demonstrate the presence in the aqueous extract of a peroxidase, which is easily destroyed by boiling, and is without action on tyrosin, in the absence of tyrosinase. It also possesses the properties of a catalase, for on placing 20 c.c. in a eudiometer tube over mercury, in contact with hydrogen peroxide, 12 c.c. of oxygen are liberated in a few hours.

The dialysed extract is neutral to litmus, and neither gives the xanthoproteic reaction, nor the usual colouration given by proteins when heated with Millon's reagent. When heated to boiling, in presence of acetic acid, it becomes opalescent, and a small quantity of coagulated matter separates from it.

By extraction with alcohol Spence obtained a more active peroxidase; after evaporating the alcohol from the extract, the enzyme forms a vitreous mass. In aqueous solution it is active only in presence of hydrogen peroxide, and this activity is destroyed by the addition of mineral acids or alkalies, potassium cyanide, sodium fluoride, or mercuric chloride.[1] On exposure to air and light, it becomes inactive, but is not destroyed, for boiling does not cause it to disappear, even after forty minutes.

On the subject of the chemical nature of this enzyme Spence has made the following observations:—Although it contains a good deal of nitrogen it shows none of the reactions of the proteins, but gives the pyrrol reaction; after fusion with potash it reduces Fehling's solution, and gives the pentose colour-reaction with phloroglucinol and hydrochloric acid, this being in accordance with observations made by Bach and Chodat, Cazeneuve, Tschirch, and Stevens. This reaction must be due to the association with the enzyme of a certain carbohydrate group.

The presence of a peroxidase in the insoluble constituent of rubber, therefore, appears to be beyond doubt; but in what relation do these two bodies stand to one another?

As Bach and Chodat hold, the peroxidase is inactive, and cannot bring about a colouration, such as the darkening of rubber, in the absence of an oxygenase or a peroxide.

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[1] The optimum temperature of the oxygenase-peroxidase of rubber appears to be about 55° C.

Spence sought to ascertain whether there were not an oxygenase present in the insoluble. He obtained only negative results with aqueous or alcoholic extracts, but when he introduced small fragments of crude rubber into the extract, in presence of tincture of guaiacum he obtained the characteristic blue colouration; the rubber must, therefore, contain an oxygenase, which gets destroyed in the various extraction processes, or which is not easily set free from the large amount of colloidal material with which it is associated. Experiments already referred to, made direct with latex, resulted in the isolation of this oxygenase.

The aqueous extract of the insoluble matter, separated from the latex, gives, in fact, all the positive reactions in the absence of hydrogen peroxide, and the conclusion may be drawn that a complete oxidase (oxygenase peroxidase) is present in the rubber.

Spence maintains that if, in a latex, the rubber were first caused to coalesce, and then, whilst still in that condition, thoroughly washed with water, containing a little formic acid, or heated to 90° C.,[1] and finally coagulated, a rubber would be obtained which would neither darken nor become tacky. Rubber prepared in this way contains only 0·17 per cent. of nitrogen, equivalent to 1 per cent. of protein, whereas rubber from the same latex (*Funtumia*), prepared by the ordinary methods, contains 0·85 per cent. of nitrogen or 5·3 per cent. of protein. The latter is found coagulated in the wash-waters. Spence's observations, it is easy to see, are of very great importance from the point of view of the preparation, the colour, and the keeping qualities of rubber, since the enzymes, which have been shown to be the great offenders, can be readily removed.

It is obvious, as pointed out by Bertrand, that under the influence of light the effect of the enzymes becomes increasingly detrimental. Victor Cayla,[2] like Spence, has found oxidising diastases in the rubbers of *Ficus Carica*, *F. elastica*, *F. prolixa Vogelii*, *Euphorbia Cyparissus*, *E. sylvatica*, *Castilloa*, *Manihot*, *Landolphia*, and *Marsdenia verrucosa*.

In a later investigation on the discolouration and tackiness of Castilloa rubber,[3] Spence attributes these phenomena solely to the action of enzymes. He showed that the part played by these was essentially catalytic—that is to say, they do not start the reaction, but they influence its velocity once it is started.

In the following table the protein content of various rubbers is given :—

PROTEIN CONTENT OF VARIOUS RUBBERS.

Kind of Rubber.	Protein.	Kind of Rubber.	Protein.
	Per cent.		Per cent.
Crêpes, I., . . .	2·41	Manaos, . . .	4·56
Kassai—Black, . .	4·30	Congo Clusters, . .	4·51
,, —Red, No. 1, .	1·06	Negro, . . .	0·98
,, — ,, ,, 2, .	2·12	Fine Para, . . .	2·41
Uellé, . . .	4·11	Upper Congo, . .	5·21
Maniçoba, . . .	8·63		

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[1] This is the process employed in Java, as recommended by De Brunes, who washed the coagulum at a temperature of 90° C., and thus obtained almost colourless rubber.

[2] *Le Caout. et la Guttapercha*, 1908, 5, 2185.

[3] *Analyst*, 1912, 37.

We shall have occasion to refer, later, to the fact that these proteins are capable of fixing a certain amount of halogen, the figures given by Blum and Vaubel being :—

Bromine, ...	4 to 5 per cent.
Iodine, ...	6 to 7 ,,
Chlorine, ...	2 to 3 ,,

Clayton Beadle and Stevens[1] have indicated a new method of separating the insoluble matter from rubber. This consists in heating the latter gently with phenetole until dissolved, and pouring the solution into benzine, when the insoluble matter is rapidly deposited.

From this somewhat confused assemblage of investigations on the insoluble constituent—a confusion resulting from the discussion which has raged between various protagonists, each energetically defending his own ideas and hypotheses—it would appear that the substance is not a simple one, but contains several widely different constituents. These are :—

(1) Nitrogenous substances, in the proportions indicated, and comprising :—

(*a*) Oxidases or co-ferments, the existence of which in presence of air is very probably the main determining cause of tackiness or stickiness ;

(*b*) Nitrogenous crystalloids in very small quantity, probably derived from the serum. These are the compounds isolated by Spence, and to the examination of which he has devoted special attention.

The separation of the nitrogenous constituents of rubber is difficult, and cannot be effected with absolute completeness.

(2) Oxidised rubber, or at least a substance containing oxygen which, on Weber's hypothesis, might be a polyprene hydrate, $C_{30}H_{48}$, $10H_2O$, representing the last traces of an intermediate compound in the process of formation of rubber from cellulose.

(3) Hydrocarbons with the same fundamental molecule as rubber—$C_{10}H_{16}$—but in a different state of polymerisation. That is to say, if rubber be represented by $(C_{10}H_{16})_n$, these hydrocarbons would have the formula $(C_{10}H_{16})_{n+q}$. Such is the complex, the presence of which was pointed out by Seeligman some years ago.

Whereas the protein constituents remain constant in quantity, as might be expected, that does not seem to be the case with the other constituents.

The oxygen compounds of rubber increase in a remarkable way when the freshly precipitated rubber is left exposed to the air, and the super-polymerised complex is liable to increase in quantity, more particularly under the influence of light.

The whole question of the insoluble constituents must, however, be regarded as still in a very unsettled state, necessitating much further study before our knowledge of the subject is complete.

Thus far we have considered the various impurities which may be present in raw rubber, and the means adopted for their removal and estimation. It will now be well to consider the rubber hydrocarbon itself, to study the forms of chemical combination into which it is able to enter, and the methods for its direct determination which have been based upon them; then to

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[1] *Zs. Chem. Ind. Koll.*, **1912**, **11**, 61-65.

explain how the preparation of derivatives has led up to the determination of its structural formula and constitution.

At the outset of these investigations it was to the action of heat that recourse was had, because it was wrongly supposed that rubber was unattackable by all reagents.

This crude method, although it allowed of the isolation of isoprene, the parent hydrocarbon of rubber, gave results which, from the analytical point of view, were not of much interest.

This is not surprising, for, as found by Harries,[1] rubber decomposes *in vacuo* at temperatures between 25° and 300° C., and the products which can be separated are very different from those which enter into the composition of the substance.

The caoutchene, eupione, heveene, amylenes, and butylene which are thus obtained do not pre-exist in the polyprene molecule; they are all formed by the action of heat upon its liberated component parts, for their molecular arrangement is different in the rubber molecule.

When we come to consider, later on, the synthesis of rubber and the preparation of isoprene, we shall have occasion to refer to the work of Barnard, Gregory, Dalton, Himly, Greville Williams, Cloez and Girard, and especially to that of Bouchardat and Tilden; for information on products other than isoprene, derived from rubber, we can only refer the reader to the book by Seeligman, Falconnet, and Torrilhon, in which are to be found all details of interest in connection with these bodies; these are, moreover, well known to most chemists.

Wallach's work on the terpenes, and the preparation from them of crystalline derivatives, with definite melting points and otherwise perfectly characterised, by the action of bromine, nitrous acid, and nitrosyl chloride, led Gladstone and Hibbert,[2] about the year 1888, to study the action of the halogens, Cl, Br, and I, on rubber.

On passing chlorine into a solution of rubber in chloroform they obtained a dichloro-hexachloride in the form of a white powder—$C_{10}H_{14}Cl_2Cl_6$. Under similar conditions, bromine gave two derivatives—viz., $C_{10}H_{16}Br_4$ and $C_{10}H_{15}Br_5$. The first of these is a simple addition product, whilst the second, which is a partly substituted derivative, is formed, according to Gladstone and Hibbert, by the following reaction:—

$$C_{10}H_{16}Br_6 = C_{10}H_{15}Br_5 + HBr.$$

The hexabromide could not be isolated.

The substitution product is obtained either by evaporation of the solvent or by precipitation with ether, but it undergoes change on drying. Iodine was found by these authors to have no action on rubber under the same conditions.

Weber took up this investigation again in 1900, and the results obtained by him are given in his paper on the "Nature of Rubber."

With bromine he was able to prepare a stable tetrabromide, which he precipitated from the chloroform solution by means of alcohol, and which could be dried without decomposition. The presence of ammonium thiocyanate facilitates precipitation. On analysis this bromide gave Br = 69·93 per cent. $C_{10}H_{16}Br_4$ requires Br = 70·17 per cent.

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[1] *Moniteur Scientifique*, 1910, 24.

[2] *Trans. Chem. Soc.*, 1888, 53, 679.

It sometimes happens that the chloroform solution, after the addition of bromine, becomes converted into a jelly which cannot be brought into solution again. The dry bromide extracted from the jelly does not differ in composition from the normal bromide, but it is absolutely insoluble in all solvents. The normal bromide of rubber is soluble in chloroform, although its solutions have always a colloidal appearance. It is absolutely insoluble in hydrocarbons, ethyl acetate, acetic anhydride, and carbon disulphide; it is slightly soluble, in the hot, in aniline, pyridine, and quinoline, and is soluble in piperidine, but with partial decomposition.

When the dry bromide is heated at 30° to 60° C. it becomes yellow, and gives off HBr; at a higher temperature the decomposition is more rapid, and results, finally, in the production of a dark brown mass; decomposition is not, however, complete, for even after prolonged heating at 150° C. bromine still remains.

Alcoholic soda has only a slight action on it, and it is only partially attacked by sodium ethylate under pressure at 100° C.

The tetrabromide is indifferent to the action of mineral acids. Fuming H_3PO_4 only acts upon it slowly, and boiling solutions of chromic acid, or of a chromic-sulphuric acid mixture, are without action.

The tetrabromide is, in fact, a remarkably stable compound.

Making use of the researches of Gladstone and Hibbert and Weber, Budde and Axelrod[1] proposed, independently though simultaneously, two methods for the determination of rubber with the aid of the tetrabromide.

In Axelrod's process 1 grm. of rubber is dissolved by heating it for three hours in an oil bath with 100 c.c. of petroleum spirit; to the solution 100 c.c. of a solution of 6 grms. of bromine and 1 grm. of iodine in 1,000 c.c. of carbon tetrachloride are added, and the tetrabromide is thus precipitated; 150 c.c. of 90 per cent. alcohol are now added, and the whole is allowed to stand for four hours, when the tertabromide is filtered on to a tared filter, washed with a mixture of alcohol and tetrachloride, then with alcohol alone, dried at 60° C., and weighed. The filter and contents are then incinerated, and the weight of the ash is deducted from the first weight; this gives the weight of pure tetrabromide, which when multiplied by the factor 0·314 gives the weight of rubber.

An objection to this method is that at 60° C. the drying of the tetrabromide is incomplete, and moreover it suffers from the general defect of tetrabromide methods in giving too low results, for the reasons set forth by Harries.

Budde's first method consisted in dissolving the rubber in carbon tetrachloride, filtering the solution, and brominating by means of 50 c.c. of the solution described above; after standing for six hours absolute alcohol was added, and the bromide filtered off, washed, dried, and weighed.

This process was criticised by Fendler and Kuhn, who maintained:—

(1) That the solution of the rubber in the tetrachloride at ordinary temperatures was incomplete;

(2) That the time allowed for bromination was too short.

They proposed to substitute for tetrachloride boiling toluene, and to extend the period of bromination to 24 hours. The toluene treatment should facilitate the separation of the insoluble impurities which always react with bromine, although, according to Manasse, they are negligible.

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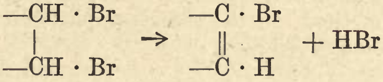
[1] *Gummi Zeit.*, 1909, 24, 1205, 1229.

Budde then modified his method, by reducing the amount of sample taken to 0·2 grm., prolonging the digestion for 24 hours, and doing away with filtration altogether. The precipitate formed on the addition of absolute alcohol was decomposed with fuming nitric acid in presence of a known quantity of silver nitrate solution, the excess of the latter being afterwards determined by titration with ammonium thiocyanate. The amount of combined bromine could then be calculated, and from this the amount of rubber in the original sample.

Although it is more practical than previous processes, this method still lends itself to criticism.

It takes no account of the error arising from the presence of protein, which it is difficult to remove completely, even by means of repeated purification of the rubber, and which combines, according to Beck,[1] with 4 to 5 per cent. of bromine.

Harries and Rimpel[2] state, on the other hand, that they have always noticed that appreciable quantities of hydrogen bromide are produced during bromination. It might be objected that this is due to the presence of resins, or other secondary substances in the rubber; but the fact is that the hydrogen bromide is formed even in the case of chemically pure rubber; not only, then, does the halogen add on to the caoutchouc molecule, but a secondary reaction occurs. Either the ready-formed bromide breaks down into an unsaturated bromide and HBr:—



$$\begin{array}{l}\text{—CH}\cdot\text{Br}\\ \quad|\\ \text{—CH}\cdot\text{Br}\end{array} \rightarrow \begin{array}{l}\text{—C}\cdot\text{Br}\\ \quad\|\\ \text{—C}\cdot\text{H}\end{array} + \text{HBr}$$

or a substitution product is formed by the direct action of bromine on the caoutchouc.

From these considerations one may suppose that the product which Budde regarded as a tetrabromide of caoutchouc is, rather, a lower bromide, and, if that be so, it is only natural that his results should be low.

There is also another possibility—viz., that, in addition to the bromide which is insoluble in alcohol and tetrachloride, another soluble bromide is formed.

By evaporating the filtrate from an analytical operation *in vacuo*, Harries and Rimpel isolated a red oil, containing crystals, and which evolved hydrogen bromide when exposed to air. On drying this *in vacuo* over sulphuric acid and potash, until its weight was constant, they obtained a solid, dark brown residue, soluble in carbon disulphide and precipitated from its solution by petroleum ether. If this product, after purification, be regarded as tetrabromide, and its weight be added to that of the insoluble tetrabromide in order to calculate the rubber content, a figure greater than 100 per cent. is invariably obtained. This seems to show that the soluble bromide is richer in bromine than the initial tetrabromide; it may possibly be Gladstone's hexabromide.

Spence and Galletly[3] sought to bring about the decomposition of the rubber bromide by other means than the use of nitric acid and silver nitrate, as proposed by Budde in his revised process. They found that by heating

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[1] *Le Caout. et la Guttapercha,* 1912, 9, 6029. [2] *Gummi Zeit.,* 1909.

[3] *Le Caout. et la Guttapercha,* 1911, 8, 5313.

the bromide with a mixture of sodium carbonate and potassium nitrate more satisfactory results could be obtained.

Their method of procedure was as follows :—0·5 grm. of the tetrabromide was mixed with 1 grm. of the alkaline mixture in a platinum crucible; a layer of the carbonate-nitrate mixture was placed on top, in order to avoid any loss of hydrobromic acid. The crucible was heated gradually to redness for half-an-hour, care being taken not to allow the contents to become liquid. After cooling, the melt was dissolved in water, the solution filtered, and the halogen present determined gravimetrically, or by Carius' method. For the mixture of potassium nitrate and sodium carbonate Spence and Galletly substituted, successively, a mixture of the two carbonates, and then sodium carbonate alone, working at a dull red heat; the results obtained were a little higher than when using the mixture of nitrate and carbonate, but the authors regard them, nevertheless, as satisfactory.

They recommend that before precipitation with silver nitrate the melt should be made strongly acid with nitric acid.

The sample to be analysed should be prepared with care, and the tetrabromide mixed very carefully in a mortar with the carbonate, or mixture of nitrate and carbonate.

Spence maintains that this process, which is much simpler, gives much more accurate results than the ordinary Budde method. This appears to us to be hardly probable for the points open to criticism are the same in the two methods.

On comparing the results obtained by Budde's method with those obtained by Harries' nitrosite method, on the same samples of rubber, the following marked differences are observed :—

ESTIMATION OF RUBBER CONTENT.

KIND OF RUBBER.	RUBBER CONTENT.	
	Nitrosite Method.	Bromide Method.
	Per cent.	Per cent.
Guayule—Crude, . .	88·80	70·20
Ceylon Sheet, . . .	96·00	88·80
Congo—Crude, . . .	92·09	85·30
Para—Pure, . . .	101·80	86·10
,, ,, . . .	99·40	91·80

It will be seen at once that the values obtained by the two methods differ in every case to an extent which cannot be put down to manipulative error.

Budde's method, then, even as modified by Spence, does not give sufficiently accurate values to be regarded as a quantitative process. Nor is it possible to correct the results obtained by it by introducing a constant (about 10 per cent.), for since we do not know how bromine behaves with the different rubbers, this constant could not be regarded as absolute.

The action of the proteins and resins, if the rubber is not perfectly purified, may stand for much in these results.

One can understand the very vigorous criticism of this process by Hinrichsen,[1] for the purer the rubber used, the greater seems to be the amount of hydrogen bromide evolved.

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[1] *Chem. Zeit.*, 1911.

Hübener having in view, more especially, the analysis of vulcanised samples, has attempted to modify this process by treating the rubber direct with bromine water on a sand bath. His process also has been very strongly criticised by Hinrichsen and Memmler, in their book, entitled *Der Kautschuk und seine Prüfung*, from which we shall find frequent occasion to quote.

Hübener has put up a lengthy defence in the *Chemiker Zeitung*, and from his numerous replies, which we shall not analyse because they deal mainly with vulcanised rubber, we propose to quote only one passage, which expresses a very curious idea :—" The rather general mistrust in the method of determining rubber as bromide, is due mainly to the presence of protein. The reason why irreproachable results are not always obtained is chiefly that the cells of protein retain within them small globules of rubber, on which neither the disaggregating agents nor the brominating solution can act, because they are unable to diffuse through the semi-permeable membrane of protein."

However that may be, from the practical standpoint the bromide method is less and less used, and, according to Brock,[1] different figures are obtained by the Fendler process, as well as by the Budde method.

Prior to 1900 iodine was supposed to be without action on rubber, and this view was shared by Gladstone and Hibbert, whose memoir is certainly the most important one which had been published at that time on the subject of the reactions of rubber.

Nevertheless, Weber was able to prepare an iodide of rubber, by the action of a concentrated solution of iodine in carbon bisulphide on a 3 per cent. solution of rubber in the same solvent.

The two solutions were left in contact for 24 hours, and shaken from time to time. The solution became a jelly; this was filtered through silk gauze into excess of alcohol, and the product was washed with the same solvent until free from every trace of free iodine, and finally dried *in vacuo* at 50° C.

The compound thus obtained is a yellowish-brown powder, slightly soluble in ordinary solvents, and only dissolving in aniline and piperidine when heated, and then with partial decomposition. When exposed to light iodine is slowly liberated from it, and its colour darkens; heating at 100° C. produces the same effect.

The analysis of the product gave the following results :—$C = 22{\cdot}93$; $H = 3{\cdot}08$; $I = 72{\cdot}03$ per cent.; $C_{20}H_{32}I_6$ requires $C = 23{\cdot}21$; $H = 3{\cdot}09$; $I = 73{\cdot}09$ per cent.

It is very remarkable to find that rubber, which was said to be unacted upon by iodine, actually forms compounds containing 72 per cent. of that halogen.

In spite of the interesting nature of Weber's observation, no practical use seems to have been made of it, doubtless on account of the instability of the hexaiodide. Weber also studied the action of the halogen acids, more particularly hydrogen chloride and hydrogen bromide, upon rubber.

When hydrogen chloride was passed through a solution of rubber in chloroform, different results were obtained, according to whether moisture was present or not. With the dry gas it was found impossible to obtain a product of constant composition, the chlorine varying from 11 to 18 per cent. in different experiments. The reaction is evidently incomplete, since the hydrochloride $C_{10}H_{16} \cdot HCl$ requires $Cl = 20{\cdot}22$ per cent. The dry gas seems to have a peculiar action, from the standpoint of repolymerisation,

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[1] *Le Caout. et la Guttapercha,* 1912, 9, 5945.

on tacky or sticky rubbers. We have already stated that this action has been observed in the case of reclaimed rubbers, and it is noteworthy that rubbers treated in this way appear to absorb, on vulcanisation, a very considerable amount of sulphur without losing their elasticity to any extent.

It would be of interest to carry out investigations in this direction.

When moist hydrogen chloride gas is used the reaction begins very vigorously, but gradually slows down, and ceases altogether after ten to twelve hours. Towards the end the solution turns brown and becomes more limpid; if it be then poured into alcohol white clots are precipitated, which on prolonged washing become hard and brittle, and, when dried *in vacuo*, form a white friable mass fairly soluble in cold chloroform, insoluble in other solvents, and soluble with decomposition when heated with aniline, pyridine, or piperidine.[1]

The following results were obtained on analysis :—C = 57·12; H = 8·15; Cl = 33·67 per cent. $C_{10}H_{18}Cl_2$ requires C = 57·41; H = 8·62; Cl = 33·97 per cent. The substance is, therefore, a dihydrochloride of rubber. As in the preparation of all hydrochlorides of terpenes, it is necessary here also to keep the temperature as low as possible throughout the process, and never allow it to exceed 10° C. At 40° C. the dihydrochloride begins to lose HCl, and dissociation proceeds with diminishing velocity until there remains only about 20 per cent. of HCl in the residue; at this point the temperature may be raised to 100° C. without any further change taking place, which seems to show that the monohydrochloride which has been formed is a very stable substance. In spite of the comparatively convenient nature of the process, the conversion of rubber into hydrochloride does not appear to have found application in analysis.

Working, under conditions similar to those just explained, with hydrogen bromide and iodide, Weber was unable to produce hydrobromides and hydriodides analogous with the hydrochlorides of rubber.

The only known action of hydriodic acid on rubber is the one discovered by Berthelot, who found that at 180° C. the result of the interaction of these two substances is to bring about a break-down of the rubber molecule, and the formation of hydrocarbons of high boiling point. Of this fact Pickles made use in his discussion with Harries on the constitution of dimethyl-*cyclo*-octadiene.

The utilisation of the nitrogen oxide derivatives of rubber had formed the subject of many memoirs, and had enabled simple and certain methods of estimation to be devised, before the ozonides were isolated by Harries. As early as 1892[2] Henriques, in his work on the analysis of rubber, had suggested the use of fuming nitric acid in estimations, "which completely oxidises the rubber, converting the carbon into carbon dioxide and the hydrogen into water." (This statement has been contested, for oxalic acid is also produced.)

In 1901[3] Harries published his earliest observations on the action of nitrous fumes on rubber.

"All chemists know that rubber stoppers are vigorously attacked by

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[1] When hot hydrochloric acid is used to destroy textile fibres in the process of reclaiming rubber, a rubber hydrochloride is formed which is quite insoluble in ordinary solvents, such as benzine, turpentine, and petroleum ether. The "nerve" of the rubber seems at the same time to be improved. It can be converted into a more soluble form by heating it with acetic acid.

[2] *Chem. Zeit.*, 1892, 16, 1595.

[3] *Ber.*, 1900, 33, 779.

nitrous fumes; nothing has, to my knowledge, been published about the yellow amorphous compound, containing nitrogen, which is formed under these circumstances."

Dissolving rubber in light petroleum, Harries passed through the solution a current of nitrous gas produced by the action of nitric acid on arsenic; a colloidal mass was first formed, but after a time this was transformed into a golden yellow magma, which could easily be filtered off. This substance was soluble in ethyl acetate, and could be precipitated from the solution in a granular form by the addition of ether; its purification was, therefore, possible.

On heating, it softened between 95° and 100° C., and gradually decomposed, gas being evolved at about 135° C. It was readily dissolved by weak alkalies, and was thrown out unchanged from these solutions by mineral acids.

On analysis the following figures were obtained:—$C = 44{\cdot}5$; $H = 5{\cdot}9$; $N = 13{\cdot}3$ per cent. $C_{10}H_{16}N_2O_3$ requires $C = 56{\cdot}6$; $H = 7{\cdot}6$; $N = 13{\cdot}2$ per cent.

These figures do not agree with the composition of a nitrosite, $C_{10}H_{16}N_2O_3$, and Harries, therefore, thought the substance might be a polynitrosate (?) of the empirical formula $C_{40}H_{62}N_{10}O_{24}$. In 1902 Harries resumed these experiments and obtained some very remarkable results, which he set forth in two papers "On the Chemistry of Para Rubber."

Harries succeeded in obtaining, successively, three different nitrosites, and the conclusions which can be drawn from the formation of these compounds have been of singular assistance in throwing light upon the constitution of rubber, as will be seen later. In these experiments Harries started with Para rubber, purified by three successive processes of solution in benzene, and precipitation with alcohol, followed by drying *in vacuo* over sulphuric acid.

Treatment with nitrous gases was carried out with solutions containing 11·5 grms. of rubber per litre of dried benzene.

The first nitrosite—*Nitrosite A*, $(C_{10}H_{16}N_2O_3)_n$—is prepared by passing into the benzene solution a current of gaseous nitrous oxide, dried over calcium chloride and phosphoric anhydride; a pale green precipitate is obtained, which after washing with benzene and drying *in vacuo* forms a somewhat friable, greenish solid. It is decomposed without melting, by heating to 100° C.; it is insoluble, in common with the nitrosites of the terpenes, in alkalies, ethyl acetate, acetone, alcohol, ether, and benzene and its homologues. It dissolves, on heating, in aniline and pyridine, but not without decomposition. Its composition, as revealed by analysis, is:—$C = 54{\cdot}12, 55{\cdot}37$; $H = 7{\cdot}39, 7{\cdot}18$; $N = 12{\cdot}01, 12{\cdot}01$ per cent. $C_{10}H_{16}N_2O_3$ requires $C = 56{\cdot}60$; $H = 7{\cdot}55$; $N = 13{\cdot}21$ per cent.

On suspending the solid in benzene, and again passing the gas for two to three days, the nitrosite—like that of terpinene—gradually undergoes a change; its colour and solubility alter, its weight increases markedly, and gas is liberated from it.

It is then readily soluble in ethyl acetate and acetone, and it reduces Fehling's solution on heating. When purified by solution in ethyl acetate and precipitation by ether, and dried *in vacuo*, it forms a pale yellow powder, which decomposes, without melting, at about 130° C.

Analysis gave:—$C = 39{\cdot}71, 40{\cdot}53$; $H = 5{\cdot}10, 5{\cdot}75$; $N = 13{\cdot}77, 13{\cdot}07$ per cent. $C_{10}H_{15}N_3O_8$ requires $C = 39{\cdot}34$; $H = 4{\cdot}92$; $N = 13{\cdot}77$ per cent. The molecular weight of this compound, determined by the boiling point method of Landsberger-Rüber, in acetone or ethyl acetate, was found to be 568·2; $C_{20}H_{30}N_6O_{16}$ requires 600. The prolonged action of nitrous oxide has, therefore, converted the complex $(C_{10}H_{16}N_2O_3)_n$ into a C_{20} molecule; this nitrosite Harries called *nitrosite B*.

When this substance was heated with nitric acid (sp. gr. 1·4) it dissolved with frothing and evolution of red vapours. When the latter ceased to be given off the solution was poured into water; yellow flakes were precipitated. This substance when purified by repeated solution in ethyl acetate and precipitation with ether, formed a deep yellow friable powder, somewhat like nitrosite B. Analysis gave the following results:—C = 42·69; H = 5·97; N = 12·25 per cent. $C_{20}H_{31}N_5O_{14}$ requires C = 42·48; H = 5·48; N = 12·39 per cent.

The molecular weight in acetone was 591·5, the above formula requiring 565.

This substance appears to be derived from *nitrosite B* in the following way:—$C_{20}H_{30}N_6O_{16} - HNO_3 + H_2O \rightarrow C_{20}H_{31}N_5O_{14}$.

If the acid filtrate be concentrated to the consistency of a syrup by heating it at 40° C. *in vacuo*, and the residue be taken up in ethyl acetate, crystalline oxalic acid is obtained, together with a pale yellow oil, soluble in water, turning brown with alkalies, and giving, when neutralised with ammonia, a yellow, sparingly soluble silver salt with silver nitrate. This oil appears to contain, as its chief constituent, a nitrated fatty acid.

When a solution of *nitrosite B* in dilute potash is heated at 80° C. with a 2 per cent. solution of potassium permanganate, and the manganese dioxide filtered off, a syrup is obtained, from which oxalic, succinic and butyric acids can be isolated. The action of moist nitrous acid is very different from that of the dry gas, and it was by the use of the moist gas that Harries was able to isolate *nitrosite C*, the third nitrosite. This is formed on passing the moist gas into a benzene solution of rubber for a long time; the mass heats up, acquires an oily consistency, and, at the end of two or three days, solidifies to a voluminous, golden yellow mass. This is filtered off, washed with benzene, and purified by dissolving it in ethyl acetate and reprecipitating with ether, and repeating the process twice. The precipitate forms, when dry, a yellow powder, which decomposes without melting between 130° and 160° C.

Analysis gave:—C = 42·87, 42·74, 42·78; H = 4·78, 5·47, 5·31; N = 14·32, 14·20, 14·21 per cent. $C_{20}H_{30}N_6O_{14}$ requires C = 41·52; H = 5·23; N = 14·53 per cent.

The molecular weight, in acetone solution, was 651; $C_{20}H_{30}N_6O_{14}$ requires 578. This substance does not dissolve in alkalis without decomposition, and it gives off nitrous acid; on heating with amyl alcohol it is converted into a substance having the formula $C_{20}H_{38}N_4O_{12}$.

Nitrosite C strongly reduces Fehling's solution, and is oxidised by nitric acid or permanganate to products very similar to those obtained from *nitrosite B* under the same conditions.

Harries repeated the preparation of the substance a large number of times, and satisfied himself that, by observing always the same experimental conditions, he always obtained a product answering, pretty closely, to the composition $C_{10}H_{15}N_3O_7$, with a double molecule.

These very curious experiments of Harries led him to devise a method for the determination of true rubber in crude and vulcanised rubbers, by means of the formation of *nitrosite C;* this experimental method has given rise to various observations, which we propose to analyse.

In June, 1902, Weber[1] also attempted to prepare nitrosites by the action of nitrous gases on benzene solutions of rubber. He obtained a substance with the formula $(C_{10}H_{16}N_2O_3)_n$, similar, that is to say, in composition to Harries' *nitrosite A*, but differing from it materially in properties. Returning to his original method of preparation of *nitrosite C*, Harries perfected the process, and succeeded in obtaining a product of constant composition, the formula of which $(C_{10}H_{15}N_3O_7)_2$ has been very definitely confirmed. He proceeds in the following way:—a current of nitrous oxide is passed into a benzene solution of purified rubber, which has been allowed to stand for 24 hours; after 24 hours' passage of the gas a yellow, friable precipitate, soluble in ethyl acetate, is formed. This is collected, washed with benzene, and dissolved in ethyl acetate; this solution is treated again with nitrous gas till saturated, after which the solvent is evaporated *in vacuo* at 30° C., and the residue poured into absolute ether; it is purified by three times dissolving and precipitating.

Analysis gave the following:—$C = 40{\cdot}65$; $H = 5{\cdot}71$; $N = 14{\cdot}58$ per cent. $(C_{10}H_{15}N_3O_7)_2$ requires $C = 41{\cdot}52$; $H = 5{\cdot}19$; $N = 14{\cdot}53$ per cent.

The molecular weight, by boiling-point method, in acetone was found to be 561, the calculated value being 578.

In the course of these experiments Harries made several interesting observations. Thus he found that *nitrosite A* when left in contact with ethyl acetate, saturated with nitrous fumes, is converted into a very pure *nitrosite C*. The product thus obtained has a sharp decomposition point between 158° and 162° C.—that is to say, between the same temperature limits as the nitrosite of dimyrcene, a substance studied by Harries, and, according to him, closely allied to the nitrosite of rubber. This new *nitrosite C* gave the following results on analysis:—$C = 41{\cdot}85$; $H = 5{\cdot}37$; $N = 14{\cdot}64$ per cent. $(C_{10}H_{15}N_3O_7)_2$ requires $C = 41{\cdot}52$; $H = 5{\cdot}19$; $N = 14{\cdot}53$ per cent.

As regards *nitrosite B*, Harries perceived in conformity with the observations of Mauthner and Suida,[2] that the nitrous acid, in passing over the calcium chloride employed to dry it, was converted into nitrosyl chloride, and that he should have obtained a product similar to the one prepared by Weber by treating a benzene solution of rubber with this compound—a product of which we shall speak in a moment. These first experiments had reference to Para rubber; when repeated[3] with rubbers of different origins, with very impure sorts—such as Guayule—with latex, such as that of *Landolphia Heudelotii*, they gave identical results, and Harries even applied them, with equal success, to guttapercha, to balata, and to industrial rubbers.

The product from Mozambique rubber decomposed at 161° C., and gave $C = 41{\cdot}07$; $H = 5{\cdot}42$; $N = 14{\cdot}39$ per cent.

That from Guayule—an exceedingly impure and very tacky rubber—gave very similar results, decomposing between 158° and 160° C., and giving $C = 42{\cdot}76$; $H = 5{\cdot}49$; $N = 14{\cdot}08$ per cent.

The compound from gutta gave $C = 41{\cdot}13$; $H = 5{\cdot}43$; $N = 13{\cdot}97$ per cent., and that from balata gave $C = 43{\cdot}27$; $H = 5{\cdot}74$; $N = 13{\cdot}67$ per cent. $(C_{10}H_{15}N_3O_7)_2$ requires $C = 41{\cdot}52$; $H = 5{\cdot}19$; $N = 14{\cdot}53$ per cent.

The method of determining rubber by means of the nitrosite, under the conditions laid down by Harries, has become almost classical, and is used to characterise different rubbers, in conjunction with the ozone method, and

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[1] *Ber.*, 1902, 35, 4429.

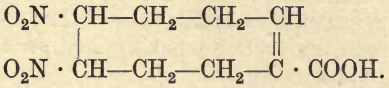
[2] *Monatsh.*, 1894, 15, 107.

[3] *Ber.*, 1902, 35, 1937.

in preference to the tetrabromide method, because the information furnished by it is nearer to the truth.

Alexander—who has devoted much attention to all matters concerning rubber, and whose competence to speak from both the technical and the scientific point of view cannot be questioned—published, about 1907, a paper in which he summarised his work on the application of Harries' method to the determination of caoutchouc in rubbers, by means of nitrosites.[1] The nitrous acid used by Alexander was obtained either by heating lead nitrate or by the action of nitric acid on starch, methods which yield mainly N_2O_4, and differ from that employed by Harries, who used nitric acid and arsenic, which yield chiefly N_2O_3.

By the action of this gas on benzene solutions of various rubbers he obtained in every case a product $C_9H_{12}N_2O_6$, which differs in composition from Harries' *nitrosite C*. Alexander called this product a *nitrosate*, and ascribed to it the following constitution :—



This brownish-yellow substance decomposed between 90° and 100° C., instead of between 158° and 162° C.; it was very soluble in acetone and ethyl acetate, and was precipitated from these solutions by benzene, alcohol, water, and carbon tetrachloride. It was also soluble in caustic alkalies and in solutions of sodium carbonate, and was precipitated from these solutions unchanged by mineral acids.

Since the formula of rubber contains C_{10}, the formation of a product $C_9H_{12}N_2O_6$ ought to be accompanied by the liberation of carbon dioxide, and this Alexander observed to be the case.

In spite of this difference in composition, from the point of view of the determination of rubber, the results were the same, and were equally constant, whether Harries' formula or that of Alexander were taken for calculation.

Alexander attributed the differences which he pointed out, in the first place, to the way in which he purified the rubber used in his experiments, and secondly to the method of preparation of the nitrous acid used by him.

Alexander's results do not invalidate in any way the method of estimation devised by Harries, since the rubber content obtained by the two methods is the same, although arrived at by the use of different factors. These results have, however, been contested by Harries, and by his pupils, Gottlob and Korneck,[2] who have both carried out very detailed investigations of the nitrosite process.

Gottlob[3] states that Alexander has departed from the experimental conditions laid down by Harries (1) in the preliminary treatment of the rubber, (2) in the choice of solvent, (3) in the preparation of the nitrous gas, and (4) in the process of drying, and that for these reasons he could not obtain results identical with those obtained by Harries; he, nevertheless, recognises that the action of a nitrous acid, of which the N_2O_4 content may vary, may give rise to different nitrosites, but he maintains that by using

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[1] *Ber.*, 1907, 40, 1070.

[2] O. Korneck, *Gummi Zeit.*, 1910, 25, 77.

[3] *Z. S. f. anal. Chem.*, 1907, 20, 2213.

an excess of acid all of them can be converted into the *nitrosite C* of Harries. The low melting point he attributes to the presence of acetone, which is difficult to eliminate, Harries' compound behaving in the same way in presence of acetone.

Alexander did not accept this view of the matter, and the discussion on the subject is not yet closed. Without going into details, which have no important practical bearing, Alexander's summing up of the position, as set forth in the *Zeitschrift für angewandte Chemie*, 1911, p. 680, may be quoted:—"Can the reaction between nitrous acid and rubber be utilised for the determination of the latter? Nitrosation under definitely fixed conditions gives rise to a quantity of crude nitrosite, which is always a little more than twice that of the rubber taken. As there is no difficulty in maintaining the required conditions, this constancy of weight of the nitrosite obtained justifies the conclusion that this reaction can be utilised for the determination of rubber."

In our opinion, in spite of all the discussion, the method of estimating rubber by means of nitrosites is a practical one, and sufficiently accurate as an indication of the amount present; on this the opinion of the opponents, with the exception of Esch, is unanimous. It is, therefore, the only point which need be adhered to.

Various chemists have investigated the action of other oxides of nitrogen on rubber. Thus Ditmar,[1] following up the work of Henriques, to which we have already referred, has devoted attention to the action of fuming nitric acid on rubber.[2] He found that the action was very violent, flame being produced, whilst the temperature rose to 96° C. and remained there. On cooling it was found that, with the exception of traces of carbon, solution was complete. When the solution was filtered through glass wool, and largely diluted with water, a granular, reddish-yellow substance was precipitated. This substance was soluble in ethyl acetate, from which it was precipitated by the addition of ether. After purification it was dried *in vacuo* over sulphuric acid; it appeared to be homogeneous, and its weight represented 22 per cent. of the rubber originally taken. It sintered, without definitely melting, at about 142° to 145° C., and decomposed at a higher temperature. It was soluble in paraffin, quinoline, ethyl acetate, nitrobenzene, and benzaldehyde; insoluble in water, ether, chloroform, petroleum ether, alcohol, and benzene. It dissolved in caustic alkalies, forming a blood-red solution, comparable with that obtained by treating colophony with nitric acid and dissolving the product in alkali. It had an acid value of 8·62.

Analysis gave:—$C = 46{\cdot}30$; $H = 5{\cdot}03$; $N = 11{\cdot}35$ per cent. $C_{10}H_{12}N_2O_6$ requires $C = 46{\cdot}87$; $H = 4{\cdot}68$; $N = 10{\cdot}93$ per cent. The molecular weight, in ethyl acetate solution, was 250; $C_{10}H_{12}N_2O_6$ requires 256.

Ditmar attempted to acetylate this product, by heating it with acetic anhydride; he obtained an orange-coloured powder, soluble in alcohol and in acetone, and precipitated from solution by ether. This substance had the following composition:—$C = 48{\cdot}32$; $H = 4{\cdot}69$; $N = 9{\cdot}39$ per cent.

$CH_3 \cdot COO \cdot (C_{10}H_{11}O \cdot N_2O_4)$ requires $C = 48{\cdot}32$; $H = 5{\cdot}06$; $N = 9{\cdot}13$ per cent.

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[1] *Ber.*, 1902, 35, 1401.

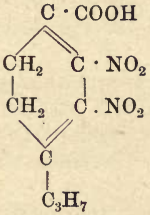
[2] The action of nitric acid had been tried before Henriques by Berniard, Hare, Trommsdorf, and Schwanest.

The product is, therefore, a mono-acetyl derivative. On saponification a yellow, flocculent precipitate was formed.

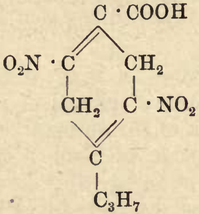
On reducing the acetyl derivative with stannous chloride in a sealed tube at 100° C., Ditmar obtained a brown powder, which is an amido compound, the nitrogen being present in the compound $C_{10}H_{12}N_2O_6$ in the form of two nitro-groups.

$$C_9H_{11}(COOH)(NO_2)_2+6SnCl_2+12HCl = C_9H_{11}(COOH)(NH_2)_2+6SnCl_4+4H_2O.$$

The products resulting from the action of HNO_3 on rubber appear to be cuminic acid derivatives, dinitro-dihydrocuminic acid, a ring compound of which two isomers may be present, viz. :—



and



5·6 dinitro – 2·3 dihydrocuminic acid. 3·6 dinitro – 2·5 dihydrocuminic acid.

Terry made an attempt to utilise the colouration produced when the solution obtained by the action of nitric acid on rubber is made alkaline with soda, for the determination of rubber colorimetrically. A standard tint is prepared by treating a known weight of pure rubber in the manner indicated, and with this the colour of the solution obtained with the sample under examination is compared. The method is analogous to Eggertz' method of estimating carbon in steel analysis.

The series of reactions which has just been summarised seems to point to the occurrence of depolymerisation, followed by the conversion of the fundamental rubber hydrocarbon into an aromatic compound. Harries[1] has also investigated the action of nitric acid on rubber, and his results confirm those of Ditmar.

The elementary composition, and the molecular weight of the compounds obtained point to the formula $C_{10}H_{12}N_2O_6$; but this substance constitutes only a small proportion of the products of the action of nitric acid on rubber. By concentrating the mother liquors *in vacuo* a yellow oil is obtained, from which, on the addition of ethyl acetate, oxalic acid is precipitated, in quantity corresponding with about two atoms of carbon per $C_{10}H_{16}$ molecule. The residual product obtained on evaporation of the ethyl acetate is an acid oil, giving a brown solution with alkalies, only slightly soluble in water, and, after neutralisation with ammonia, yielding a yellow silver salt—$C_6H_8NO_5 \cdot Ag$—by double decomposition.

The reduction in the number of hydrogen atoms in the initial product, brought about by the action of nitric acid on rubber, led Harries at the time to suppose that the latter contained a cyclic nucleus, which might well be either dihydro- or tetrahydro-cuminic acid.

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[1] *Ber.*, 1902, 31, 3256.

The action of nitrosyl chloride and of nitrogen peroxide on rubber was investigated by Weber.[1]

In the former case isoamyl nitrite and acetyl chloride were added to a solution of rubber in benzene. In ten minutes the solution was converted into a stiff jelly, which was clear at first, but soon became cloudy through the liberation of minute bubbles of gas, which rapidly increased in size and swelled up the whole mass. The swelling ultimately subsided and the mass liquefied, becoming at the same time darker in colour. The liquid could now be filtered, but left no appreciable residue on the filter. On adding absolute alcohol to the filtrate a colloidal mass, as elastic as untreated rubber, separated. This was found on analysis to contain a small proportion of chlorine and only traces of nitrogen. The jelly rapidly decomposed, yielding a product similar to rubber in physical properties, but differing from it in some chemical properties.

Contrary to Weber's hopes, nitrosyl chloride did not give with rubber, as with the terpenes, a crystalline product, with definite melting point; the study of the product obtained was not pursued by Weber from the analytical point of view.

With nitrogen peroxide—N_2O_4—Weber obtained more interesting results. On passing nitrogen peroxide, obtained by heating lead nitrate, into a 1 per cent. solution of purified Para rubber in benzene, an amorphous product was formed, which, when shaken, was thrown down as a granular powder. It is difficult to free this substance from occluded nitrogen dioxide. On adding water to an acetone solution of the substance a finely flocculent yellow precipitate is formed, which after washing and drying *in vacuo* forms an amorphous, friable mass, soluble in acetone, ethyl acetate, acetic acid, acetic anhydride, ethyl formate, epichlorhydrin, nitrobenzene, aniline, and ethyl alcohol; but insoluble in methyl alcohol, ether, chloroform, benzene, carbon disulphide, and carbon tetrachloride. It decomposes without melting at about 112° C., turning dark brown, deflagrating, and leaving a voluminous residue of carbon. On analysis the following figures were obtained:—$C = 52{\cdot}5$; $H = 7{\cdot}1$; $N = 12{\cdot}75$ per cent. $C_{10}H_{16}N_2O_4$ requires $C = 52{\cdot}6$; $H = 7$; $N = 12{\cdot}71$ per cent.

The compound is soluble in ammonia in the cold, and in dilute caustic alkalies and methyl alcoholic soda on heating. When ethyl alcohol is added to the latter solution a brown, flocculent, sodium salt is precipitated—$C_{10}H_{15}N_2O_4 \cdot Na$—from which a silver salt—$C_{10}H_{15}N_2O_4 \cdot Ag$—a brown gelatinous substance can be obtained by double decomposition.

In 1903[2] Weber proposed to apply this process, in preference to the nitrosite method of Harries, to the determination of caoutchouc in raw and vulcanised rubbers; he insists upon the constancy of the results obtained, the variation being less than with *nitrosite C*, and upon the rapidity with which the operation can be carried out, and gives supplementary details as to the control of the process, as follows:—The N_2O_4 is prepared by heating lead nitrate, 20 grms. of the latter being sufficient for one analysis. The gas is dried by passing it over glacial phosphoric acid, and its passage through the benzene solution of the rubber is continued until the latter has assumed a very marked brownish-red colour.

After allowing it to stand for an hour, the product forms a deep yellow coherent mass, which is filtered off, dried, and dissolved in acetone on the

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[1] *Ber.*, 1906, 35, 1947.

[2] *Ber.*, 1903, 32, 3103.

water bath. The deep yellow solution thus obtained always has a little grey scum floating on it, consisting of mineral impurities, together with the protein from the rubber. These can be filtered off on a tared filter and their amount determined. The acetone solution is then poured, in a thin stream, into eight times its volume of water[1]; the nitro compound separates in bright yellow flocks, and is collected on a tared filter, washed, dried at 90° C., and weighed.

100 parts of this precipitate correspond, exactly, with 59·65 parts of rubber hydrocarbon; the factor 0·6 is usually employed in calculations. The rubber is thus determined by direct weighing. In the insoluble residue the mineral matter may be determined by ashing a weighed quantity, and in another portion the protein may be estimated by determining the nitrogen by Kjeldahl's method. Resins should be determined in the original sample, and the extracted sample, dried in a current of coal gas, used for the determination of rubber, etc. As will be seen, Weber's method permits of a fairly rapid analysis of crude rubber, which is all but complete—only the determination of the insoluble impurities being lacking.[2] But in spite of its advantages it has not come into common use, like the nitrosite and tetrabromide methods.

Alexander, after carrying out a certain number of experiments, following Weber's method strictly, maintains that his formulæ are not accurate, and that it is impossible to obtain the same results, working with the same rubbers. Neither Harries nor Alexander admitted Weber's dinitro formula —$C_{10}H_{16}N_2O_4$—holding that it is not in accordance with facts. In support of this view Harries puts forward the work on *nitrosite C*, which we have already dealt with.

He then showed that the same nitrosites can be obtained from very different rubbers, and, repeating Weber's experiments, showed that, with N_2O_4, compounds are obtained which are closely related to the nitrosites, and not dinitro-caoutchouc. According to Esch, Harries' method is less certain than Weber's, and the results are always too high.

"So far," he says,[3] "no analyses have been published which justify Weber's method, in which the red oxides of nitrogen are used for the determination of rubber."

It is stated that Fendler found that Harries' nitrosite method and that of Weber, gave the same results. Surprise is justifiable, for the gases used are different, $N_2O_3 + NO$ being used by Harries, and N_2O_4 by Weber. Esch[4] deduced from his experiments that if all the red oxides of nitrogen do yield the same addition products with rubber, on the other hand neither the quantity of nitrosite obtained nor its composition are constant.

It follows that if one applies this method in a complete analysis, even employing Alexander's formula, $C_9H_{12}O_6N_3$, from which 1·9984 grms. of nitrosite corresponds with 1 grm. of rubber, one obtains yields exceeding 100 per cent.

Calculating the percentages from the results given by Alexander,[5] the following figures are obtained :—

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[1] Instead of water a salt solution may be used. Alexander employs a 10 per cent. solution of ammonium chloride.

[2] According to Weber, this method gives different results with natural and reclaimed rubbers, and can be used to distinguish between them.

[3] *Gummi Zeit.*, 1904.

[4] *Le Caoutchouc et la Guttapercha*, 1909, 6, 1204.

[5] *Gummi Zeit.*, 1907, 21, 730.

SAMPLES.	RUBBER.	"NON-NITROSABLE."	TOTAL.
	Per cent.	Per cent.	Per cent.
Para, Fine, ...	107·7	0·3	108
Caucho, ...	109	0·2	109·2
Mangabeira, ...	105	0·1	105·1
Lower Congo, ...	115·5	0·8	116·3
Guayule, ...	99·6	6·4	106

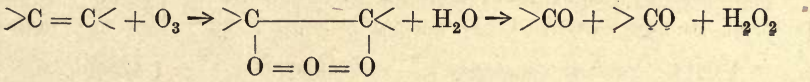
The methods of direct estimation of rubber by means of the oxides of nitrogen lend themselves, therefore, as do the bromide methods, to considerable criticism. Must they be regarded as giving an indication rather than an accurate determination of the amount of rubber? The subject is still open to discussion.

Amongst the other inorganic compounds which interact with rubber must be mentioned sulphur dioxide, which, as observed by Reychler in 1908, is absorbed by rubber, forming an unstable sulphite, readily decomposed by heat. Isoprene, it may be noted, yields a similar compound when treated with sulphur dioxide.

It was natural that Harries, who, in conjunction with his pupils, and in particular Langheld and Hæffner, has devoted much attention to the study of the ozonides, especially those of the terpenes, should be led to investigate the action of ozone on such a complex molecule as that of rubber. None of the methods hitherto employed for the progressive breaking down of the molecule—such as permanganate and nitric acid—had given positive results, as will be shown in studying the constitution of rubber. With the aid of ozone the desired object was achieved, and this method of decomposition has given results of the highest interest.

In a series of prior researches Harries had established the fact that when unsaturated compounds are treated with ozone, either direct, or in aqueous solution, a molecule of O_3 is added on at each double bond.

The ozonides thus obtained, which are explosive substances, are converted by heating with water into aldehydes or ketones, hydrogen peroxide being simultaneously produced :—



$$>C=C<+O_3\rightarrow\begin{array}{ccc}>C & \text{———} & C<\\ | & & |\\ O & =O= & O\end{array}+H_2O\rightarrow>CO+>CO+H_2O_2$$

To ozonise rubber Harries proceeded as follows :[1]—A 1 per cent. solution of purified rubber in chloroform was taken, and into it for ten hours was passed a current of ozonised air, containing 6 to 12 per cent. of ozone; the end of the reaction was ascertained by the decolourisation of bromine.[2]

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[1] The ozonisation of rubber was attempted, prior to Harries, by Wright. (*Bull. Soc. Chim.*, 1897, 18, 438.)

[2] *Ber.*, 1904, 37, 2708. This work was carried out in conjunction with Reuter, Langheld, Hans, and Müller. As the result of more recent work, Harries saw the necessity of purifying the ozone used by washing it with caustic soda and sulphuric acid, which absorb the oxyozone which is formed together with ozone.

The solution was evaporated *in vacuo*, at 20° C., on a water bath to the consistency of a syrup, and was then dissolved in ethyl acetate, and precipitated with petroleum ether. A very thick oil, solidifying to a vitreous mass, was thus obtained; this was the ozonide, which in this form is explosive.

The product has none of the characteristics of rubber; it is soluble in alcohol, ethyl acetate, and benzene, but insoluble in petroleum ether, and these solubilities are utilised in its purification; like ozone, it acts upon the photographic plate.

Analysis of a sample which had been four times dissolved in ethyl acetate and precipitated by ether, gave the following results:—

C = 48·84, 49·06, 47·76, 51·76, 52·39 per cent.
H = 6·90, 6·95, 6·71, 6·79, 7·0 per cent.

$C_{10}H_{16}O_3$ requires C = 65·21, H = 8·75 per cent.
$C_{10}H_{16}O_6$ „ C = 51·72, H = 6·90 „
$C_{10}H_{16}O_9$ „ C = 42·84, H = 5·76 „

from which it is clear that each $C_{10}H_{16}$ group had added on two molecules of ozone. The molecular weight was found to be about 526, $(C_{10}H_{16}O_6)_2$ requiring 464; on account of the difference between these two figures it may be said that it is not proved that the substance is quite homogeneous and does not contain the molecular group $(C_{10}H_{16}O_6)_3$. In any case it is certain that it is a product of the depolymerisation of the large rubber molecule. It is to be noted that the ozonide thus obtained always contains a little chlorine, derived from the chloroform employed as solvent, and the last traces of which it is impossible to remove.

The ozonide is dissolved in water and the solution boiled. After a short time the solution is found to possess the following properties:—

(1) It reduces Fehling's solution and ammoniacal silver nitrate.

(2) With alkalies a brown colouration is produced, and resinous substances are formed.

(3) It gives a strong pyrrol reaction with ammonia and acetic acid.

(4) On boiling, irritant vapours are produced.

(5) Hydrogen peroxide is present.

These reactions are characteristic of the formation of the keto- and di-aldehydes, of the levulinic aldehyde and succinic aldehyde studied by Harries.[1]

The physical constants of levulinic aldehyde are as follows:—Boiling point at 10 mm. = 18·7° C. at normal pressure = 66° to 68° C.; density $\frac{4^\circ}{25^\circ} = 1{\cdot}0814$; optical constants $n_d^{21{\cdot}5^\circ} = 1{\cdot}42567$; $n_\alpha^{21{\cdot}5^\circ} = 1{\cdot}42359$; $n_\gamma^{21{\cdot}5^\circ} = 1{\cdot}43658$; $M\,R_D = 25{\cdot}14$; $M\,R_{\gamma\,.\,\alpha} = 0{\cdot}68$.

Its structural formula is

$$CH_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CHO$$

that is to say, it is a γ-ketonic aldehyde.

It is not very stable, and polymerises under the influence of acids and alkalies; it yields a di-semicarbazone, crystallising in white scales, soluble

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[1] Harries and Bœgemann, *Ber.*, 1909, 42, 439.

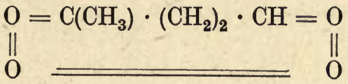
in methyl alcohol, and melting at 178° to 180° C.; a di-*p*-nitrophenylhydrazone, crystallising in brown scales, melting point 106° C. With phenylhydrazine it gives a phenylmethyldihydropyridazine crystallising in pale yellow needles, melting point 197° C.; with *p*-nitrophenylhydrazine hydrochloride it yields nitrophenylmethyldihydropyridazine; and with pyruvic acid and β-naphthylamine it forms γ-ketobutyl-2-naphthocinchonic acid, yellowish needles melting at 290° to 291° C.

The substance can, therefore, be very definitely characterised, chemically.

With benzenesulphydroxamic acid it does not yield hydroxamic acid; it only gives very little acetal when acted upon by orthoformic ether, or iminoformic ether hydrochloride; and only resinous products are obtained from it on bromination.

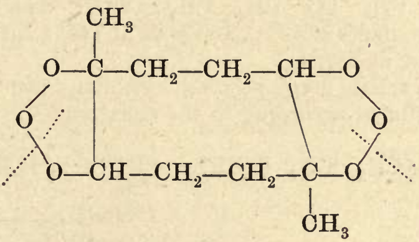
When reduced with aluminium amalgam, in ethereal solution, it gives a mixture of amylglycol 1·4, and a product with a very high boiling point, which seems to be the anhydride of acetylpropyl alcohol.

By the somewhat prolonged action of boiling water levulinic aldehyde gives levulinic aldehyde peroxide, a substance which crystallises in microscopic scales, soluble in alcohol, ethyl acetate, and caustic alkali. This substance gives a sparingly soluble silver salt, liberates iodine from iodides, decolourises indigo and permanganate solutions, and reacts with Fehling's solution and ammoniacal silver nitrate. It has the following structure :—[1]

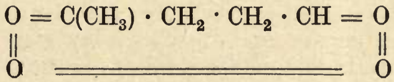


$$\begin{array}{ccc} O & = C(CH_3)\cdot(CH_2)_2\cdot CH = & O \\ \| & & \| \\ O & =\!=\!=\!=\!=\!=\!=\!= & O \end{array}$$

The ozonide would have the following structure (the rubber complex $(C_{10}H_{16})_n$ having been broken down to a simple molecule) :—



and would give, on splitting up across the dotted lines :—



$$\begin{array}{ccc} O & = C(CH_3)\cdot CH_2\cdot CH_2\cdot CH = & O \\ \| & & \| \\ O & =\!=\!=\!=\!=\!=\!=\!= & O \end{array}$$

Levulinic aldehyde peroxide.

$$+ CH_3\cdot CO\cdot CH_2\cdot CH_2\cdot CHO$$

Levulinic aldehyde.

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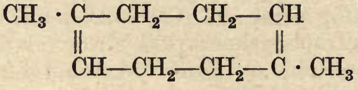
[1] Harries, *Ber.*, 1905, 38, 1195.

The formula of rubber would thus be :—



Since the rubber molecule is symmetrical the substance is optically inactive, a point to which we shall return in discussing its constitution. Without adhering to the method of isolating and characterising the aldehydes formed on hydrolysis, Harries pursued another method of analysis.

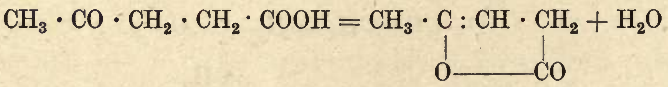
He found that if the ozonide be heated for a long time with boiling water, under a reflux condenser, it dissolves completely, and the hydrogen peroxide reaction is no longer shown, that substance having oxidised the aldehydes to the corresponding acids. If the solution be then distilled the volatile products which have escaped oxidation—viz., acetone and levulinic aldehyde —pass over with the steam ; the latter can be readily identified in the distillate, by means of its phenylhydrazine derivative, which melts at 197° C. The residue constitutes a pale yellow syrup, in which crystals soon form, melting at 195° C.

On distilling this residue at a reduced pressure of 10 mm., almost pure levulinic acid passes over at 140° to 150° C., in quantity equal to about 70 per cent. of the theoretical ; the acid is identified by means of its phenylhydrazone, which crystallises well and melts at 108° C. The analysis of the latter gave :—$C = 65{\cdot}59$; $H = 7{\cdot}44$; $N = 13{\cdot}53$ per cent. $C_{11}H_{14}N_2O_2$ requires $C = 64{\cdot}02$; $H = 6{\cdot}84$; $N = 13{\cdot}62$ per cent.

If the temperature of distillation be raised to 170° to 190° C. a new decomposition sets in, and crystalline succinic acid is obtained ; this can be identified by distilling its ammonium salt with zinc dust, when the pyrrol reaction is obtained.

Levulinic acid, $CH_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot COOH$, which is isomeric with methyl acetoacetate, melts at 32° C. and boils at 144° C. at 12 mm., and under atmospheric pressure at 239° C.

It undergoes partial decomposition, yielding two isomeric lactones, *α* and *β* angelic lactones, according to the equation :—



Both are soluble in water, alcohol, and ether.

With hydriodic acid it gives normal pentanoic acid ; and it forms the usual ketone derivatives with hydroxylamine and phenylhydrazine.

It is reduced by sodium amalgam to γ-hydroxyvaleric acid.

It is oxidised by nitric acid, in the warm, to acetic, malonic, and succinic acids and carbon dioxide.

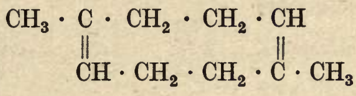
Under the influence of light it decomposes, yielding acetic and propionic acids.

With hydrogen cyanide it forms a ring compound, the nitrile of methylglutalactonic acid ; with benzaldehyde β-benzylidene-levulinic acid.

The electrolysis of an alkali salt gives 1 : 4, diacetylbutane.

It will be seen, therefore, that the substance is readily characterised.

Since, when ozone acts on rubber, aldehyde and aldehyde peroxide are first formed, and then levulinic acid, Harries concluded that there must be two double bonds in the simple molecule ($C_{10}H_{16}$) :—



$$\begin{array}{lcccc} CH_3 \cdot & C & \cdot\, CH_2 \cdot CH_2 \cdot & CH & \\ & \| & & \| & \\ & CH & \cdot\, CH_2 \cdot CH_2 \cdot & C & \cdot\, CH_3 \end{array}$$

This complex doubtless occurs, he observes, two or three times in the molecule of ozonide, linked up by the residue from which the crystalline acid is derived.

It is noteworthy that no trace of oxalic acid is found in any of these reactions, although it is always present in oxidation by other agents than ozone; it is, therefore, not a direct product of decomposition. From this progressive degradation of the caoutchouc molecule, which could not be brought about by permanganate or nitric acid, Harries drew very interesting conclusions with regard to its structure.

Willstätter and Veraguth, by work in other directions, have confirmed the value of the somewhat unusual formula—cyclo-octadiene—given to caoutchouc by Harries.

Working with gutta which, in the pure state, appears to be isomeric with caoutchouc, Harries obtained an ozonide similar to that of the latter, although decomposing in a different way when treated with water.

These two materials differ from one another, not only in the number of $C_{10}H_{16}$ rings which go to make up the complete molecule, but also in the way in which these rings are united to one another; they are, that is to say, isomeric.

It would be interesting to know whether the different kinds of natural rubber yield different ozonides, which in turn yield different products of hydrolysis; if that were the case a simple method might be at hand of distinguishing between them.

This subject has been investigated by Gottlob, who studied the action of ozone on various African rubbers. He went to work in the following way:—The rubber was freed as completely as possible from resins and insoluble matter, and dried *in vacuo* over sulphuric acid. It was then dissolved in chloroform and ozonised. The ozonide, obtained by evaporation *in vacuo* at 20° C., was purified three times, and then distilled from solution in water. The distillate, containing the levulinic aldehyde, was treated with phenylhydrazine, giving the crystalline phenylmethylpyridazine, which could be separated by filtration, dried, and weighed.

The residue in the distilling flask contained levulinic acid and levulinic aldehyde peroxide. It was filtered, and an aliquot part evaporated until the peroxide separated quantitatively. This substance was then purified by crystallisation, dried, weighed, and identified by its melting point. The residue from the preceding operation contained the levulinic acid, which was recovered by evaporation *in vacuo* at 120° to 130° C., identified by its melting point and that of its phenylhydrazone, then dried and weighed.

The values obtained in this way differ little amongst themselves as the following table shows. Five grms. of ozonide were taken in each experiment:—

Kind of Rubber.	Levulinic Acid.	Levulinic Aldehyde.	Peroxide.	Resins.	Total.
Liana Kappa Uganda, coagulated by heat,	2·58	1·74	...	0·10	4·42
Central Uganda (Plant unknown),	2·75	1·22	0·20	0·20	4·37
Lamu Balls,	2·20	1·35	0·35	0·25	4·15
Liana Nausaly, coagulated with common salt,	2·35	1·27	0·20	0·35	4·17
Liana Nausaly, coagulated by heat.	2·30	1·36	0·25	0·22	4·13
Uganda, Interior,	2·53	1·21	0·22	0·20	4·27
Liana Kappa,	2·50	1·34	0·23	0·20	4·27
Funtumia Elastica,	2·70	1·48	...	0·20	4·38
Upper Congo, Mongala Bands,	2·35	0·97	0·25	0·20	3·77
Lower Congo, Red Thimbles.	2·23	1·48	0·20	0·30	4·21
Congo, Djuma, Red,	2·45	1·30	0·20	0·35	4·30
Upper Congo, Black Kassai,	2·64	0·96	0·32	0·30	4·22
Loanda Gankum Spindles,	2·90	1·24	0·20	0·10	4·44
Upper Congo, Equateur,	2·50	1·39	0·25	0·20	4·34
,, Lake Leopold,	2·40	1·28	0·25	0·30	4·25
,, Ordinary,	2·40	1·04	0·20	0·57	4·21

The mean values of all these results are as follows:—

Levulinic acid,	2·49	per 5 grms. of ozonide.	
Levulinic aldehyde,	1·29	,,	,,
Levulinic aldehyde peroxide,	0·19	,,	,,
Resin not decomposed,	0·25	,,	,,
	4·22	,,	,,

The average yield is 4·22 grms. per 5 grms. of ozonide, because there is always some escape of oxygen on the decomposition of the ozonides, and under this head a loss amounting to about 0·21 grm.

The analysis, therefore, accounts for only 80 to 90 per cent. of the ozonide.

As will be seen from these experiments, it is possible thus to distinguish, fairly sharply, between African rubbers and Para grades.

From the account given of these different methods of investigation established by the ingenuity of a number of workers, the conclusion will be drawn that it is to-day a somewhat simpler matter to set about the analysis of rubber, in spite of its complexity, than it was in Heinzerling's day. Although at the moment it is only in Holland that an official Bureau of Analysis has been set up, such useful control will be established sooner or later in France, a country which is one of the largest consumers of rubber.

Vernet[1] has given a very clear account of the various characteristics which it is advisable to determine in a crude rubber, and it is worth while, we think, reproducing them.

1. Country and district of origin, botanical source, methods of collection, coagulation, drying, dispatch, and packing.
2. Gross weight at the time of dispatch, gross weight at the time of sampling; tares.

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[1] *Le Caout. et la Guttapercha,* 1912, 9, 6312.

3. Physical appearance of the rubber, whether loaves, block, ball, crêpe, sheet, lump, scrap, thimbles, etc. Average colour, thickness, whether any signs of tackiness are shown.

4. Method of sampling; starting with slices through the loaf in three dimensions.

5. Loss on washing, content of technically washed rubber, with an indication of the method of washing, and of its thoroughness; content of washed and dried rubber; appearance and colour of washed, dried rubber. Examination and analysis of wash-waters.

6. Content of soluble resins and their nature.

7. Oxygen content of the washed rubber.

8. Nitrogen and protein content of the washed rubber; examination and characterisation of the proteins.

9. Content of mineral matter; examination and analysis of ash.

10. Resistance of the rubber to an oven temperature of 55° C.; degree of tackiness.

11. Plasticity of the washed rubber, by Michelin's method, or Breuil's *elastodurometer*.

12. Viscosity.

13. Elasticity.

14. Adhesive power on evaporation of solutions.

15. Dynamometric tests, giving tensile strength per square mm. of cross-section, elongation at break, and permanent elongation; tests to be made at ordinary and at different temperatures.

16. Resistance to compression and shock.

17. Measurement of expansion.

18. Determination of pure caoutchouc as tetrabromide, nitrosite, and ozonide.

19. Density and melting point.

20. Vulcanisation tests; proportion of sulphur necessary for normal vulcanisation, temperature indications; action of sulphur chloride.

21. Dynamometric and compression tests on vulcanised sample.

22. Action of ordinary and ultra-violet light.

23. Micrographic and "gomographic" examination.

This is obviously a very extensive programme, but on referring to the information which we have collected in the preceding pages, it will be seen that it is quite possible to carry it out, and that if it were put into operation a classification of species and qualities would be arrived at which would furnish most valuable information both to the commercial branches and to manufacturers.

In applying this system a variety of methods may be brought into use, of which, unfortunately, all are open to criticism.

Each set of tests must be preceded by washing, which eliminates mechanical impurities, such as sand, plant residues, humus, fibres, and stones, and soluble substances such as colouring matters, salts, sugars, alkaloids, and enzymes. This treatment gives technically pure rubber, which, in addition to the fundamental hydrocarbon $(C_{10}H_{16})_n$, contains additive oxidation products, or "superpolymerised" products, resins, proteins, and other nitrogenous substances, waxes, oils, and ethers.

There are three types of method of estimation available:—

1. Indirect, or determination by difference, according to the methods of Jacobsen, Esch and Chwolles, and Ditmar.

2. Direct, or precipitation methods, including those of Schneider, Fendler, and Spence.

3. Direct, by means of chemical derivatives, including the tetrabromide method of Budde, the nitrosite methods of Harries and Fendler, and the ozonide method of Harries.

An account has already been given of the indirect methods of Esch and Chwolles and of Ditmar. Jacobsen's method consists in drying the sample *in vacuo* over sulphuric acid, extracting the resins with absolute alcohol, determining nitrogen by Kjeldahl's method, mineral matter by incineration, and insoluble constituents by solution. The difference is taken as caoutchouc.

Schneider's precipitation method has been improved upon by Frank and Markwald; the rubber is dissolved in chloroform, and precipitated with alcohol.

Fendler dissolves the dried rubber, after determining moisture, in petroleum ether, and filters. The residue on the filter gives the impurities, and the rubber is obtained from the filtrate by precipitation with alcohol.

As regards the methods of analysis by means of derivatives, a number of details of the way in which these are carried out have already been given, and there is no need to mention them again. Besides these general processes the method of Henriques may be mentioned; this consists in destroying the rubber by the action of fuming nitric acid, but it is of little use except for the determination of inorganic impurities.

The presence of starchy material may be investigated by means of tincture of iodine.

At the present time the methods of the first two types, with the exception of Fendler's and Spence's methods, mainly applicable to African rubbers, have been given up, and according to Korneck,[1] determination by means of derivatives is employed.

Certain corrections which have been introduced have rendered them of real practical value, according to Harries.[2]

In the case of the nitrosites, for example, it has been shown that the high values obtained are due to concomitant formation of resin nitrosites; but since the latter are soluble in ether, whereas, according to Korneck, the rubber nitrosites are not, the separation of the two has been readily effected.

Contrary to what Spence thought, the presence of protein does not influence the determination, as in the tetrabromide process.

As regards the resins, Harries maintains that their ozonides are sharply insoluble in carbon tetrachloride and chloroform, whilst the rubber ozonide is soluble in these liquids; we have seen that this opinion has been contested.

More recent work by Paulsen[3] demonstrated that the ozone derivatives of various types of resin, such as dammar and sandarac, are precipitated quantitatively by carbon tetrachloride, and we have obtained similar results with the resins extracted from dead Borneo—that is to say, with definitely characterised rubber resins. Below is given a comparative table of results obtained by different methods with a number of different rubbers. This will help to fix in the mind of the reader the relative value of the "derivative" methods.

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[1] *Zeit. anal. Chem.*, 1911, 50.

[2] Lecture in Vienna, 1910.

[3] *Le Caoutchouc et la Guttapercha*, 1910, 7, 4177.

KIND OF RUBBER.	Extraction. (Fendler.)	Nitrosite. (Fendler.)	Nitrosite. (Harries.)	Tetrabromide. (Budde.)
	$C_{10}H_{16}$ per cent.	$C_{10}H_{16}$ per cent	$C_{10}H_{16}$ per cent.	$C_{10}H_{16}$ per cent.
Para—Pure,	93·14	102·21	95·25	83 90
,, —Crude,	91·09	93 52	88·96	82·93
,, —Ceylon,	93·27	103·02	97·81	94·31
Peruvian Ball—Washed,	94·37	102·05	96·17	93·68
,, —Crude,	77·31	89·83	83·79	78·71
Congo—Equateur,	66·11	75·34	68 85	63·14
Borneo—Washed,	72·31	78·05	72·24	69·79
Manaos,	90·21	96·52	89·40	83·99
Crêpe,	93·29	100 56	95·42	93·31
Guayule—Washed,	78·32	83·23	77·43	76·53

By way of completing the record, we also give below a series of analyses of different rubbers which have been communicated by Michelin,[1] as well as other analyses by various authors.

ANALYSES OF VARIOUS RUBBERS.

KIND OF RUBBER.	Yield of Dry Rubber.	Caoutchouc.	Resins.	Ash.	Moisture.
		Per cent.	Per cent.	Per cent.	Per cent.
Para—Virgin,	84·0	96·55	2·43	0·59	0·33
,, —C.I., pale,	83·9	96·65	2·75	0·25	0·35
,, ,, dark,	81·9	96·34	2·80	0·46	0·40
,, —Fine Madeira,	...	94·89	2·90	0·33	1·88
,, —Junca,	...	94·84	3·14	0·22	1·80
,, —Rio Cauro,	...	96·32	2·55	0·28	0·85
,, —Rio Negro, *a*,	...	96·81	2·36	0·25	0·58
,, —Upper Rio Negro, *b*,	...	96·86	2·20	0·23	0·71
,, —Uniny,	...	96·03	2·99	0·27	0·71
,, —2nd quality,	...	96·41	2·59	0·31	0·69
,, —Madeira,	...	96·69	2·38	0·31	0 62
,, —Lower Rio Negro,	...	96·83	2·31	0·30	0·50
,, —Fine, white,	...	96·99	2·40	0·43	0·18
,, ,, marbled,	...	96·14	3·15	0·27	0·44
,, ,, grey,	...	67·06	32·21	0·34	0·39
,, —Extra fine Madeira,	...	79·62	19·80	0·18	0·40
,, ,, ,,	...	55·86	43·54	0·24	0·34
,, ,, ,,	...	86·99	12·46	0·21	0·31
,, ,, Rio Cauro,	...	96·19	2·74	0·27	0·10
,, —Peruvian,	...	94·31	4·18	0·89	0·42
,, —Extra fine Madeira,	...	95·61	3·30	0·29	0·81
,, ,, Bolivia,	...	96·52	2·48	0·26	0·74
Caucho Mixture,	96·6	93·99	4·26	1·24	0·51
Castilloa—No. 1,	82·5	94·75	4·77	0·34	0·14
,, —No. 2,	88·0	93·77	5·91	0·38	0·04
Rio Mangabeira,	78·8	91·26	7·77	0·59	0·33
Para—Fine,	...	96·84	2·87	0·70	0·12
Sapium,	92·0	88·76	10·50	0·40	0·20
Pichucabo,	94·0	90·76	7·84	0·90	0·50
Contesté,	85·3	96·68	2·76	0·32	0·24
Seringa Verdadeira,	21·3	96·66	3·04	0·14	0·16
,, Torrada,	22·5	97·14	2·58	0·13	0·15
Ceara P,	...	93·30	3·87	2·00	0·83
,, Q,	...	93·31	3·77	2·80	0·84

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[1] *Le Caout. et la Guttapercha*, 1905, 5, 298.

ANALYSES OF VARIOUS RUBBERS—*Continued.*

KIND OF RUBBER.	Yield of Dry Rubber.	Caoutchouc.	Resins.	Ash.	Moisture.
Ceara R,	...	93·77	3·29	2·15	0·79
,, S,	...	93·80	3·31	2·09	0·75
,, T,	...	93·42	3·43	2·34	0·81
,, U,	...	93·96	3·37	1·88	0·79
,, V,	...	94·16	3·25	2·70	0·83
,, Garci,	...	84·02	11·60	3·79	0·55
,, E,	...	93·97	3·80	1·63	0·60
,, X,	...	91·61	4·95	2·85	0·50
,, Z,	...	93·71	4·23	1·28	0·75
Seringa Verdadeira, 1,	...	97·22	2·11	0·26	0·41
,, ,, 2,	...	96·95	2·76	0·23	8·40
,, ,, 3,	...	96·54	2·78	0·21	0·34
Tapuru—True,	...	94·10	4·86	0·49	0·55
,, —Floresta, dark, 1,	...	92·96	5·38	1·19	0·26
,, ,, ,, 2,	...	94·58	3·96	1·20	0·26
,, ,, ,, 3,	...	94·44	4·26	0·95	0·25
,, San Pedro,	...	95·82	3·22	0·77	0·19
Para—Fine San Pedro, 1,	...	96·93	2.64	0·09	0·34
,, ,, ,, 2,	...	96·05	3·07	0·27	0·61
,, ,, ,, 3,	...	93·97	5·15	0·25	0·63
,, —Extra fine, 1,	...	94·65	4·36	0·33	0·66
,, ,, 2,	...	84·80	4·39	0·30	0·51
,, —Ciudad Bolivar, 1,	...	93·27	3·60	2·89	0·24
,, ,, ,, 2,	...	72·56	2·44	24·60	0·40
,, ,, ,, 3,	...	94·64	4·67	0·59	0·15

ANALYSES OF RUBBERS BY VARIOUS AUTHORS.

KIND OF RUBBER.	Moisture.	Caoutchouc.	Resins.	Proteins.	Ash.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Mascarenhasia,	10·0	69·0	6·1	3·50	11·40
Funtumia,	1·7	84·6	6·4	6·50	0·80
Chlanda,	2·8	77·9	8·8	9·40	1·10
Landolphia,	4·9	76·2	14·1	2·00	2·80
Parameria,	...	91·8	6·3	1·50	0·50
Plectaneia,	2·0	87·0	10·0	...	0·42
Tsongonofitra,	3·62	72·5	11·0	10·63	2·25
Ficus,	7·6	89·5	3·7	0·20	...
Ceara,	4·4	67·7	4·4	20·40	3·10
Assam,	1·5	80·1	11·6	2·60	1·12
Krepioah,	1·0	91·3	4·7	0·90	0·42
Ofruntum,	7·9	78·0	5·0	7·60	1·20
Mascarenhasia,	4·05	88·17	3·01	1·89	2·88
Congo, I.,	3·0	85·8	7·4	3·50	...
,, II.,	3·4	84·0	8·2	3·70	...
,, III.,	3·1	87·5	7·6	1·50	...
Abyssinia,	1·8	84·0	7·2	...	...
Funtnmia, Af. Occ.,	0·8	90·8	7·0	2·00	...
Nigeria,	0·4	88·0	9·0	2·20	...
Periflora,	0·77	88·8	8·45	0·98	...
Pirahazo,	2·70	65·70	19·10	11·00	...

CHAPTER X.

CONSTITUTION OF RUBBER.

The problem of determining the constitution of the rubber molecule is one of the most difficult in the domain of chemical investigation. Thus it will be easily understood that its solution has taken a number of years, and that it is only quite recently, at the cost of much hard work and considerable effort, that it has been found possible to decipher its structure and to devise a formula for its fundamental molecule, without, however, being able to determine its degree of polymerisation.

Weber says, with good reason,[1] that colloidal compounds like rubber offer an altogether peculiar resistance to the attempt of investigators to determine their internal architecture, and their molecular weight.

Colloids are, in fact, as we have seen, devoid of those physical constants which serve to establish the individuality of a chemical compound. They pass by insensible gradations from the solid to the liquid or gaseous state, without definite melting or boiling point to indicate the change of state, and without sharp changes in their properties.

To characterise such substances, to separate them from their homologues or derivatives, to purify them, are likewise problems of the most complicated order, on account of the lack of well-defined compounds to serve as data for their identification. For such work reliable methods are lacking, and it becomes necessary to work them out *ab initio.*

The study of rubber offers, in a superlative degree, difficulties of this kind, and the words used by Wallach with reference to the terpenes might be applied with equal justice to this case, " Rubber is a veritable chemical enigma." Ten years ago it was scarcely possible to regard the empirical formula of rubber as absolutely established, bearing in mind the incomplete character of the analyses.

As the presence in the mass of various impurities, such as the insoluble constituents, proteins and resins had not then been determined, the presence in it of oxygen, nitrogen, chlorine, and sulphur, as claimed by Cloez and Girard, left Weber thinking before the empirical formula $C_{10}H_{16}$, and he had doubts as to its accuracy.

But even supposing these difficulties brushed aside, and assuming the empirical formula to be established, was it justifiable to regard the substance as homogeneous ? Was it formed by the polymerisation of a single $C_{10}H_{16}$ molecule, or by the polymerisation of a number of isomeric molecules, having the same elementary composition ?

Such were the questions upon which discussion was opened, and upon a good many of which it is not yet at an end.

The investigation of the physical constants having led chemists in the first place to try and obtain a definite boiling point or melting point for rubber, the study of its decomposition by heat came about quite naturally,

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[1] *J. Soc. Chem. Ind.*, 1900, 19, 215.

and although, from the analytical point of view, this may not have led to valuable results, it has, nevertheless, been responsible for the discovery of the hydrocarbon progenitor of rubber—viz., isoprene, C_5H_8.

It was, in fact, soon observed that, when heated, rubber began to decompose before melting or boiling; it was found that under the influence of heat its stability was extremely low, and that depolymerisation set in when the amount of heat applied was only slight.

Rubber cannot be distilled, even *in vacuo*, without decomposition[1]; when heated in a retort it yields a great variety of products, which pass over between 25° and 300° C.

Not only is a separation effected between the $C_{10}H_{16}$ molecules of the complex, reducing the size of the latter, but, in becoming free, these $C_{10}H_{16}$ molecules are liable to undergo internal modification of structure, yielding always hydrocarbons whose empirical formula is $C_{10}H_{16}$, but which differ in constitution from the original $C_{10}H_{16}$ group, as it exists in the rubber molecule.

There is nothing surprising about this to anyone who has studied the chemistry of the terpenes, for one of their characteristics—which have been so well defined by Wallach—is precisely this susceptibility to intramolecular change—*metamerism*—by which one compound is converted into an isomeride or *metameride* under the influence of acids and alkalies, and more particularly of heat. In order to recognise them, during the period of transformation, it is necessary to be able to isolate certain of their additive compounds, by which they may be characterised.

But other phenomena occur during the pyrogenic decomposition of rubber; indeed if those which we have just referred to were the only ones they could soon be cleared up with the aid of the methods introduced by Wallach.

Not only is the link between the individual $C_{10}H_{16}$ molecules, which holds them together to the number of *n* in the form of a complex, severed by the action of heat; not only is the internal structure of this $C_{10}H_{16}$ unit modified, but these modified molecules are themselves capable of repolymerising or of combining with one another, forming new hydrocarbons which have nothing in common with rubber, such as caoutchene, colophene, heveene, eupione, and benzene compounds. Further, the molecule $C_{10}H_{16}$ itself breaks down into smaller molecules, and these, when liberated, can recombine and form new compounds poorer in carbon, like butylene, isoprene, dimethylallene, dihydroisoprene. If, in giving rise to the new compounds, the molecule should split up, at the double bonds, into two similar fragments without further change of structure, these fragments are capable of reconstituting the original molecule by a new condensation; this is what occurs in the case of isoprene. But under the increasing influence of heat it may also happen that the molecule splits up into dissimilar fragments, and that these latter themselves undergo changes of structure at the moment of rupture. Whether these remain free, or whether they condense, one has to do with new compounds.

It will be understood, then, how great is the complexity of researches on the subject of rubber. To every hypothesis put forward there corresponds a problem to be solved; and the solution of the whole of these

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[1] *Cf.* Harries, *Chem. Zeit.*, 1910, 34, 315.

problems has required the patience of a whole generation of investigators. In studying the action of heat on rubber, what first attracted the attention of chemists, when it had been demonstrated that it was impossible to determine a definite melting or boiling point for rubber, was the property exhibited by it of decomposing, yielding a variety of compounds, which, however, were always identically the same.

These compounds, which were described generally as "*rubber oils,*" were utilised industrially almost as soon as they were discovered, in virtue of their solvent power for rubber itself, as well as for copal and other varnish gums. Then they acquired a very great importance from the scientific point of view when it was found possible to fractionate the mixture, and to isolate from it certain portions, like isoprene, which could either be converted into rubber or condensed to form terpenes. When pure Para is subjected to moderate heat, for example, it first of all becomes softer and more plastic; this property, which has been known since the time of La Condamine and Fresneau, has long been made use of in the industrial manipulation of rubber. At 145° C. its condition undergoes a change; it becomes viscous and adheres to solid bodies; it sinters and loses its elasticity. At 170° to 180° C. it melts to a thick, blackish, sticky liquid, somewhat like treacle. It has then lost all its original and characteristic physical and mechanical properties, and these can only be restored to it with very great difficulty. In spite of this apparently very profound change, it is surprising to find on analysis that it has conserved its original chemical composition, that it still remains, in fact, a $C_{10}H_{16}$ hydrocarbon.

On raising the temperature still further the rubber begins to boil, and gradually disappears, leaving no appreciable residue. The mixture of hydrocarbons thus produced possesses the singular property, first recognised by Barnard in 1833, and which we have already referred to, of dissolving raw rubber at ordinary temperatures.

Berniard in 1781 [1] was the first to distil rubber and collect the oily product; François Fourcroy, in his *Système des connaissances chimiques*, also mentions this product. Bate and Enderby, in 1834, produced it, in London, almost on an industrial scale, obtaining yields equal to 83 per cent. of the weight of rubber employed.[2] They used it in the preparation of varnish. It was their samples which were analysed by Dumas.

Jean Chevalier, Professor at the École de Pharmacie, in Paris, first gave the name of *caoutchene* to these compounds, which were afterwards studied by Gregory.

In his paper, published in 1836, with the title *On a Volatile Liquid obtained by Distillation*, Gregory states that he first obtained an oil of specific gravity 0·666 with a boiling point of 32° C. This product was, therefore, not *eupione*, which Reichenbach had detected in 1833 but very probably impure *isoprene*. From the residue Gregory obtained various substances, the existence of which had already been pointed out by Liebig. By the action of sulphuric acid he isolated a new oil, with a density of 0·670; if the mass is kept cool during the interaction with sulphuric acid, this product is obtained colourless. The second residue, washed with potash, and rectified over calcium chloride, yielded a third liquid boiling at 226° C. with an agreeable odour, greatly resembling that of turpentine.

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[1] Ditmar, *Gummi Zeit.*, 1904, 18, 1013, *et seq.*

[2] Trommsdorf maintains that a yield of 84 per cent. cannot be exceeded.

"Its composition corresponds with that of the gases from which the oil is formed."

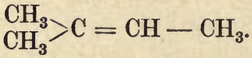
A year before Gregory's publication, Himly took up, in a very thorough manner, the study of the products of the dry distillation of rubber.

He found that 12 parts of dry rubber give 9 parts of an oily, ethereal distillate, of a brown colour, and with a disagreeable, pungent odour, and a density of 0·870.

He gave this crude product the name of *Faradayine*, in memory of Faraday, whose studies on rubber had been a guide to him in his investigations, and who had anticipated him in the extraction of a kind of ethereal oil from rubber.

This crude oil formed an excellent solvent for rubber, copal, and all the varnish resins. The separation of the various bodies produced in the reaction was first effected by Himly.[1]

Amongst the more volatile fractions, the existence was revealed of a substance with a density of 0·654, and a boiling point varying from 33° to 44° C.; this was impure isoprene, in admixture, as Ipatieff and Wittorf[2] showed in 1897, with trimethylethylene, or ordinary amylene—



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!>C = CH - CH_3.$$

In the less volatile fractions Himly found a hydrocarbon *caoutchine*, a name which was retained by Ure. He extracted this substance, in a pure state, by treating the crude oil with sulphuric acid, diluted with eight times its own weight of water. After washing, distilling over potash, treating with alcoholic hydrogen chloride, saponifying, and drying, he obtained by distilling over baryta and over metallic sodium a substance with the following characteristic properties:—Density, 0·842; vapour density, 4·461; boiling point, 170° C. This product, which appears to be a polymeride of isoprene, remains liquid at — 30° C., is insoluble in water, soluble in alcohol, ether, essential oils, and fatty oils. It resinifies when left in contact with hydrogen peroxide; it is attacked by chlorine and by bromine, yielding a viscous halogenide, with a density of 1·443, and decomposing when distilled. When treated with a base it yields a new hydrocarbon, richer in carbon. Caoutchine combines with hydrogen chloride and hydrogen bromide; the hydrochloride is isomeric with pinene hydrochloride; it forms a brownish oil with a nauseous odour, and a density of 0·950. It decomposes on distillation, but is quite unattacked by bases.

By the alternate action of bromine and sodium, caoutchine loses two atoms of hydrogen, and is converted into cymene. Sulphuric acid converts it into a thick oil, analogous with Bouchardat's *heveene*. This substance has a density of 0·921, boils at 315° C., absorbs chlorine yielding a waxy product, and is resinified by the action of sulphuric acid. To-day caoutchine is regarded as identical with Bouchardat's di-isoprene, $C_5H_8 \cdot C_5H_8$, for it is the substance obtained when isoprene is polymerised at 280° C.; it is optically inactive.

In 1834 Dalton read a paper before the Manchester Scientific Society, entitled *On Certain Liquids derived from the Distillation of Rubber*, a paper which was published by Erdmann in 1837, after Gregory's work had been

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[1] "Dict. du Caoutchouc," *Ann. Chim: Pharm.*, 16, 61.

[2] *J. pr. Chem.*, 1897, 55, 1.

published. Dalton supposed that the products of the distillation of rubber were ethylene and an oil analogous with Faradayine.

In 1837 Appolinaire Bouchardat[1] published various researches on the same subject. He decomposed rubber in a copper vessel connected with a condenser, in series with which were three flasks surrounded by various mixtures of snow and calcium chloride.

To a first distillate he gave the name of *heveene;* this was a mixture of various oils, from which he isolated one substance in particular; this had a density of 0·921 at 16° C., boiled at 250° C., was soluble in ether and in alcohol, and did not solidify at the lowest temperatures then available. The name *heveene* was then restricted to this constituent. The substance is resinified by the action of chlorine, bromine, or iodine, and on treatment with sulphuric acid gives a clear oil, boiling at 182° C., and soluble in alcohol and ether. Bouchardat believed it to be similar to Gregory's product (boiling point, 226° C.), in spite of the difference in boiling point.

The second portion of the distillate was a mobile liquid, vapourising several degrees below zero, and solidifying at — 30° C. Treatment with sulphuric acid, followed by neutralisation, gave a clear liquid, distilling at 18° C., soluble in alcohol, and having a density of 0·690.

From the final portions, by means of successive fractionations, Bouchardat ultimately succeeded in isolating a liquid which, on cooling, deposited very fine acicular crystals, melting at — 12·5° C., and boiling at 18·2° C. Its specific gravity was 0·650; it was soluble in alcohol; ether and the alkalies had no action upon it.

Bouchardat gave to this product, which was closely related to isoprene, the name of *caoutchene.*

Although Perkin states[2] that Greville Williams was the first chemist to isolate isoprene from amongst the products of destructive distillation of rubber and to characterise it, one is bound to recognise that he was anticipated in this by Himly, and above all by Appolinaire Bouchardat. Greville Williams' work is, none the less, of the very highest importance.

In 1860[3] Williams succeeded in characterising isoprene by establishing the fact that Himly's *caoutchine* was a single substance and not a mixture. In these experiments the rubber was distilled at as low a temperature as possible, in order to avoid secondary decompositions. The crude distillate had a very unpleasant odour, and contained traces of volatile organic bases derived from the protein which existed in small quantities in the rubber. It was freed from these and purified by shaking it with dilute sulphuric acid, afterwards washing with water and digesting with caustic soda. On fractionation it yielded an oil passing over between 37° and 44° C., and a second between 170° and 180° C.; the boiling points of these were lowered by further rectification over sodium. Greville Williams then obtained a liquid distilling between 37° and 38° C., to which he gave the name of *isoprene.* On analysis this gave the following figures:—C = 88; H = 12·1 per cent. C_5H_8 requires C = 88·2; H = 11·8 per cent.

Its vapour density was 2·44, its density 0·683 at 20° C. On exposure to the atmosphere for several months it became viscous, absorbed oxygen, and developed the power of decolourising indigo sulphate, and of converting

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[1] *Journal de Pharm.*, 1837.

[2] *Journ. Soc. Chem. Ind.*, 1912, 31, 616.

[3] *Phil. Trans.*, 1860, 150, 245; *Proc. Roy. Soc.*, 1860, 10, 516.

sulphides into sulphates. On fractional distillation this oxidised isoprene yielded first of all pure isoprene, and then the boiling point rose and the liquid was converted into a white, spongy, elastic mass similar to rubber. The idea involved in this reaction was taken up again later by Heinemann.[1] On analysis this substance gave C = 78·80; H = 10·70; O = 10·50 per cent. C_5H_8O requires C = 78·97; H = 10·52; O = 10·54 per cent.

The isoprene prepared in this way combined with bromine with explosive violence.

On redistilling that portion of the destructive distillate which passed over between 170° and 180° C., Greville Williams obtained a liquid boiling at 170° to 173° C., which was identical with Himly's *caoutchine;* its vapour density was 4·67, twice that of isoprene. On treatment with bromine it yielded hydrogen bromide and a red oil, which became very sticky when warmed. When dried over sodium this substance yielded a pleasant-smelling hydrocarbon, distilling at 170° to 200° C.

The residue was a yellow oil distilling at 300° C.

Williams regarded the fraction passing over at 170° to 200° C. as *cymene*, and that passing over at 300° C. as *paracymene.* The former of these on oxidation yields a flocculent substance, identical with Hoffmann's insolinic acid, and characterised by its silver salt. By the action of sulphuric acid, followed by neutralisation with lime, it yields small granular crystals of a calcium salt.

Cloez and Aimé Girard also gave their attention to the dry distillation of rubber, and claimed to have found chlorine and sulphur in the products; their work is of little importance, and they drew few conclusions from it.

In chronological order the work of Gustave Bouchardat next demands consideration.

In 1875, working under Berthelot's guidance, he took up the study of the dry distillation of rubber, which had been already begun by others, and obtained, from 5 kilos. of rubber, the following products:—

(1) Caoutchene, boiling at 14° C.
(2) Its isomeride, butylene.
(3) 250 grms. of isoprene.
(4) 2,000 grms. of caoutchine, distilling between 176° and 180° C.
(5) 600 grms. of heveene, or sesquiterpenes of the composition $C_{15}H_{24}$, isomeric with essence of copahu, distilling between 255° and 265° C.

In addition, carbon monoxide, ethylene, and methane were obtained.

The residue from the distillation consisted of hydrocarbons distilling above 360° C., and other products which decomposed on heating, yielding the three hydrocarbons already classified.

From this experiment Bouchardat[2] hazarded the conclusion that all the hydrocarbons obtained by the distillation of rubber consisted either of isoprene, or of isomerides or polymerides of that substance.

We shall revert to this very important work when dealing with isoprene, the parent material of rubber; at this point we shall merely state the conclusions drawn from it, from which interesting considerations follow.

Bouchardat says that, guided by the results obtained on reducing the camphene hydrocarbons with hydrogen iodide, and more particularly by the

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[1] Eng. Pat. 14,041 of 1910.

[2] *Bull. Soc. Chim.*, 1875, 24, 108.

formation of amylene hydride, C_5H_{12}, Berthelot[1] regarded these hydrocarbons as polymerides of a certain hydrocarbon, C_5H_8.

This fundamental hydrocarbon constitutes, so to speak, the primitive cell of all $C_{10}H_{16}$ hydrocarbons. All compounds included in this group must be capable of giving rise to its formation, by a breaking-down process, or of being reproduced from it by condensation. $C_{10}H_{16}$ compounds are derived from the C_5H_8 hydrocarbon, in the same way as compounds of the aliphatic series are derived from methane, and aromatic compounds from acetylene, or its polymeride, benzene.

But the establishment of a relationship between formulæ does not resolve a problem in metamorphosis, and Bouchardat proceeds :—"It seemed to me that it was only by synthetic experiments, starting with the C_5H_8 hydrocarbon, that the question could be settled, by the production of perfectly definite compounds resulting from changes undergone by this hydrocarbon."

Bouchardat showed, successively, that, when heated in a sealed tube, isoprene is converted into a mixture of polymerides, amongst which are colophene and caoutchouc[2]; that turpentine is analogous to di-isoprene, and that, therefore, the terpenes and isoprene are very closely related; and, lastly, that caoutchouc is only a polymeride of isoprene.[3]

Although the only proof he could offer of this was that on distilling the polymeride isoprene was regenerated, Bouchardat, by a stroke of genius, established the relationship between rubber and isoprene, and was the first to lay down the principle that it was possible to pass from the hydrocarbon C_5H_8 to the complex $(C_{10}H_{16})_n$. From the analytical point of view he established the fact that caoutchouc, or at any rate its fundamental molecule, $C_{10}H_{16}$, is formed by the condensation of two molecules of isoprene, C_5H_8.

In 1881, the polymerisation was effected of a homologue of isoprene—viz., Hoffmann's piperylene[4]—the constitution of which was determined by Thiele, in 1901, to be—

$$CH_3 \cdot CH{=}CH{-}CH{=}CH_2,$$

showing that it is a methylbutadiene. These results were confirmed by Schotten[5] in 1882.

At this time, therefore, it had been established that the isomerides of isoprene could be polymerised, like Greville Williams' hydrocarbon.

Between the years 1887 and 1906, Tilden published a number of papers on isoprene, its production and condensation. We shall deal with these fully when considering isoprene.

At this point we will only mention that Tilden prepared isoprene by breaking down terpenes, such as pinene and dipentene; that he brought about its condensation by the action either of heat or of chemical reagents such as nitrosyl chloride, and observed its spontaneous polymerisation; and, lastly, that he determined its constitution to be—

$$CH_2 : C(CH_3) \cdot CH{=}CH_2.$$

In arriving at this conclusion, Tilden was guided rather by theoretical con-

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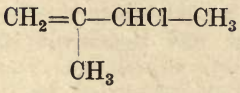
[1] *Bull. Soc. Chim.*, 1869, 9, 189.
[2] *Bull. Soc. Chim.*, 1875, 24, 108.
[3] *Comptes rendus*, 1879, 80, 361.
[4] *Ber.*, 1881, 14, 665.
[5] *Ber.*, 1882, 15, 425.

siderations than by ascertained facts. His hypothesis received a perliminary confirmation in the isolation of isoprenyl alcohol by Gadziatsky :—

$$CH_3 \cdot C(OH)\,(CH_3) \cdot CH{=}CH_2,$$

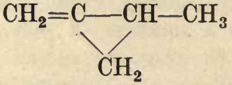
and became completely established when Kondakow obtained synthetic isoprene, starting with a compound of definitely known structure, and under conditions where all possibility of isomeric change was excluded.

By chlorinating trimethylethylene, Kondakow obtained an unsaturated chloride :—

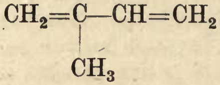


$$\begin{array}{l} CH_2{=}\underset{\displaystyle |\atop\displaystyle CH_3}{C}{-}CHCl{-}CH_3 \end{array}$$

which, on loss of HCl, can only form a trimethylene ring compound—



or a hydrocarbon of the following constitution :—



$$\begin{array}{l} CH_2{=}\underset{\displaystyle |\atop\displaystyle CH_3}{C}{-}CH{=}CH_2 \end{array}$$

that is to say, isoprene, with the structure suggested by Tilden. The product actually obtained was found to have all the properties of isoprene.

The researches of Ipatieff, Wittorf, Mokiewsky, and Euler confirmed the view which regarded isoprene as a β-methylbutadiene, 1·4, with two double bonds.

Given the fact that isoprene yields, on condensation, caoutchouc and certain terpenes, it would seem that the attempt ought to have been made, first of all, to regard rubber as a member of the terpene series, and as containing a cyclic nucleus, similar to that of pinene, in the skeleton of its fundamental molecule.

The determination of the number of double bonds in the rubber molecule could alone clear up this question, and this Weber[1] undertook to do when engaged upon the determination of molecular weight. By the action of chlorine on rubber, in chloroform solution, Gladstone and Hibbert had obtained a dichloro-hexachloride, $C_{10}H_{14}Cl_2 \cdot Cl_6$, and they claimed to have obtained, under similar conditions, an unstable hexabromide, which underwent conversion into a pentabromide ; Weber at first reached the conclusion, confirmed by the observations of optical properties made by Gladstone and Hibbert, that the caoutchouc molecule must contain three pairs of doubly-linked carbon atoms per $C_{10}H_{16}$ unit.

"If this be the case the polyprene caoutchouc must be an olefinic hydrocarbon, and not a ring compound like the ordinary terpenes ; in other words, the constitution of the polyprene would be that of an olefinic polyterpene, which would take its place at the extreme end of the series of olefinic terpenes, just as the ordinary polyterpenes do at the end of the cycloterpene series."

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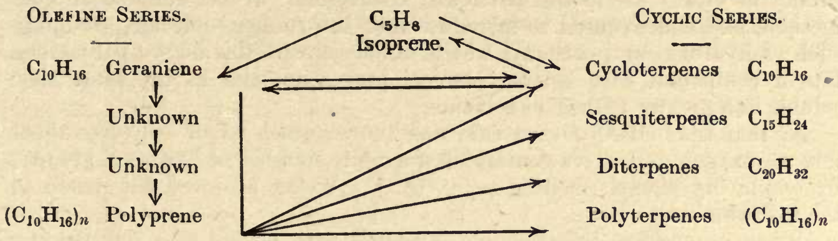
[1] *J. Soc. Chem. Ind.*, 1900, 19, 215.

The hemiterpene, C_5H_8, isoprene, would then constitute the transition stage between the two series. The following scheme expresses these relationships :—



In Weber's theory of its constitution, the fundamental molecular unit $C_{10}H_{16}$ of caoutchouc was constructed, not with the cyclic nucleus of the terpenes, but with the open chain of the olefines, like geraniene, and consequently the complex $(C_{10}H_{16})_n$ should also form an open chain. Weber remained faithful to this idea up to the time of his death, but Harries did not admit it, after his more recent work.

The study of the bromination and the isolation of the tetrabromide of caoutchouc showed Weber that Gladstone and Hibbert were wrong, and that the molecular unit, $C_{10}H_{16}$, of polyprene contained only two ethylene linkages. This was confirmed by the study of the iodides and the hydrochlorides which we have already described. This was a valuable piece of evidence, but it threw no light upon the structure, properly so-called, of the molecule $C_{10}H_{16}$, nor upon the positions of the two double bonds, the presence of which it demonstrated.

The most usual method of unravelling the constitution of a natural complex consists in subjecting the substance to carefully controlled and successive oxidations, by means, for example, of permanganate or nitric acid.

But caoutchouc is a very singular substance, in that it is not, strictly speaking, attacked by permanganate,[1] whilst nitric acid, as we have already seen, destroys it completely, converting it into products which appear to contain the benzene nucleus.[2]

Up to the time of Harries' researches it appeared to be impossible to subdivide, without internal modifications, the fundamental molecule, $C_{10}H_{16}$, into smaller, definite molecules. The method of scission indeed presents very serious difficulties. All the applications of rubber, the whole industry, are founded exactly upon the indifference of this material towards most chemical reagents.

It is true that the molecule is readily oxidised; that is a recognised fact; but, as we have seen, oxidation results in the formation of addition products, and does not appear to split up the molecule.

There remain, then, only the curious scission phenomena observed on dry distillation; but, as we have already explained, in face of the impos-

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[1] When caoutchouc in benzene solution is subjected to the action of $KMnO_4$, the solution yields on evaporation a thick colourless syrup, having none of the characteristic properties of rubber; a small amount of fatty acid can be separated from it. Analysis shows that the composition, $C_{10}H_{16}$, is unaltered, and it would appear that only depolymerisation has occurred. (Harries, *Ber.*, 1904, 37, 2708.)

[2] Ditmar, *Ber.*, 1902, 35, 1401; *Mon. Scient.*, 1902, 16, 663.

sibility of regulating this process, of the almost complete decomposition which occurs, of the intramolecular changes and atomic migrations which take place, and of the repolymerisation which goes on, the observed facts cannot be of any use in this particular connection. Weber adopted another method, and endeavoured to introduce into the rubber molecule, groupings such as hydroxyl and carboxyl which would convert this inert hydrocarbon into a compound with active chemical properties, and at the same time soluble in a greater variety of solvents.

At that time (1900) no reaction was known which would convert rubber into an oxygen derivative containing a definite number of hydroxyl groups; by employing phenol (melting point 43° C.) Weber achieved this result in the following way:—

When caoutchouc tetrabromide is heated with phenol at a temperature a little above its melting point, it may dissolve with no apparent change, but more often, even at this low temperature, a series of colour changes are observed; colourless to begin with, the liquid becomes pale green, then dirty grey, deep blue, and finally deep purple, almost crimson; the tetrabromide then dissolves completely, and a certain amount of hydrogen bromide is given off. The operation is conducted in a flask connected with a reflux condenser, and heated on a water-bath.

In order to remove all traces of unchanged bromide from the deep purple liquid thus obtained it is filtered hot through a fine cloth filter, or it is cooled and diluted with twice its volume of ether, filtered through filter paper, and the ether removed from the filtrate by distillation. The solution is then poured into a solution of caustic soda containing 50 grms. NaOH per litre, and the brown liquid obtained is heated to boiling and again filtered. On adding acetic acid to the filtrate small brownish-grey flocks are precipitated which agglomerate when the liquid is heated on a water-bath. When washed and dried the product is an amorphous mass, of the colour of buffalo-horn; it can be pulverised, and is soluble in aqueous and alcoholic alkalies, alcohol, acetone, ethyl ether, and ethyl acetate; insoluble in benzene, chloroform, carbon disulphide, and petroleum ether. On analysis the following figures were obtained:—$C = 80{\cdot}15$; $H = 7{\cdot}42$ per cent. $C_{34}H_{36}O_4$ requires $C = 80{\cdot}16$; $H = 7{\cdot}14$ per cent. These figures agree pretty closely, then, with the empirical formula $C_{34}H_{36}O_4$, and the compound may be regarded as a tetra-oxyphenyl derivative of polyprene, formed in accordance with the equation—

$$C_{10}H_{16}Br_4 + 4(C_6H_5 \cdot OH) = C_{10}H_{16}(O \cdot C_6H_5)_4 + 4HBr.$$

Seeing that Gladstone and Hibbert heated rubber, in toluene solution, to 200° C. without decomposition, it is probable that in this reaction, which takes place at 100° C., there is no scission of the fundamental molecule $C_{10}H_{16}$.

Nevertheless, it must be noted that if, during the interaction of the phenol and tetrabromide, the temperature be kept at 90° C., and the solution be afterwards treated in the manner described above, a product is obtained which, although similar to the first in appearance, gives the following analytical results:—$C = 75{\cdot}41$; $H = 6{\cdot}73$ per cent. $C_{34}H_{36}O_6$ requires $C = 75{\cdot}55$; $H = 6{\cdot}66$ per cent.

This substance would thus be a tetra-oxyphenyl-dihydroxy-polyprene:—

$$C_{10}H_{14}(OH)_2 \cdot (O \cdot C_6H_5)_4.$$

"The production of such a compound," Weber says, "is difficult to understand, and the difficulty is increased if the phenolic melt be poured into a large excess of benzene. There then separates a precipitate which may vary in colour from a dirty crimson to a deep indigo-blue. This precipitate is soluble in alcohol, acetone, glacial acetic acid, and acetic anhydride; slightly soluble in chloroform; and insoluble in ether, benzene, and carbon disulphide."

On analysis the following figures were obtained:—C = 70·09; H = 6·78 per cent. $C_{40}H_{41}O_{10}$ requires C = 70·48; H = 6·02 per cent.

This analysis is in agreement with the formula

$$C_{10}H_{16}O_5(OC_6H_5)_5.$$

When these phenoxy- or hydrophenoxy-compounds are boiled with alcoholic soda, they are all saponified, phenol being liberated. If the saponification products be washed and neutralised with acetic acid a flocculent brown precipitate is obtained, which, when dry, is soluble in caustic alkalies, alcohol, ether, acetone, acetic acid, and acetic anhydride, and insoluble in benzene, carbon disulphide and chloroform. On analysis the following results were obtained:—C = 61·11; H = 6·76 per cent. $C_{30}H_{36}O_{12}$ requires C = 61·22; H = 6·08 per cent.

When the compound is treated with alkalies it fixes still more hydroxyl groups, and gives a variety of more highly oxidised products, some of which correspond with the formula $C_{30}H_{60}O_{30}$. The repetition of this hydrolytic treatment gives products which become darker and darker in colour, and simulate more and more the behaviour of colloids.

The reaction by which they are produced is not peculiar to phenol; the cresols, carvacrol, thymol, the naphthols, resorcinol, pyrocatechol, and hydroquinone, with varying degrees of readiness, behave in the same way. With chlorophenols chlorinated reaction products are obtained, and with nitrophenols oxidised compounds. Thiophenol also substitutes itself for bromine in the tetrabromide and sets free hydrogen bromide. Anisol and phenetol are without action.

In the light of these facts there is no doubt that it is the hydrogen of the phenolic hydroxyl group which determines the point of attack in the reaction, and that the oxygen is present in the compounds in the oxide or ether condition, and not in the form of hydroxyl groups.

This very interesting study, from which other consequences follow later, contributes to the problem of the elucidation of the constitution of the rubber molecule $C_{10}H_{16}$, only a confirmation of the presence of two double bonds, which had already been revealed by the formation of the tetrabromide.

In 1902, when Harries[1] in his turn took up the study of the constitution of rubber, and carried out his work on the nitrosites, there was general agreement amongst chemists to regard rubber as a $C_{10}H_{16}$ hydrocarbon of unknown molecular weight, containing at least two double bonds to each $C_{10}H_{16}$ group, and belonging to the group of aliphatic or open-chain terpenes; such at least was the idea put forward by Weber.

The observations made by Harries, in isolating the nitrosites, tended to the justification of this theory. In acting upon rubber with nitrous acid, Harries sought to bring about the methodical decomposition or degradation

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[1] *Ber.*, 1902, 35, 3256-4429.

of the molecule, which the ordinary oxidising agents, permanganate and nitric acid, had failed to effect.

We have already seen what results were obtained by him, and how the formation of the nitrosites, and notably *nitrosite C*, has enabled an almost certain method of estimating the true caoutchouc present in crude rubber to be devised.

The decomposition of *nitrosite B* or *C* by permanganate into a series of fatty acids, in which succinic and oxalic predominate, to the exclusion of every aromatic acid, has demonstrated that, apparently, the nitrosite does not contain any carbon ring, for the products which it yields in this case are exactly similar to those yielded by an open-chain hydrocarbon, *myrcene*, a hexavalent terpene investigated by Power and Kleber,[1] and more particularly by Semmler.[2]

This analogy led Harries to study the products of the polymerisation of myrcene,[3] which are readily obtained, when the hydrocarbon is allowed to remain undisturbed for some months, or by heating it in a sealed tube for several hours at about 300° C. Two classes of product are formed—viz., volatile compounds, and those which cannot be distilled without decomposition.

The chief constituent of the former, which boil between 160° and 200° C. at 12 mm. pressure, is dimyrcene, $C_{20}H_{32}$, a colourless oil with an agreeable smell. When this is dissolved in benzene, and dry, nitrous acid is passed into the solution, a thick, red oil is first formed, which slowly solidifies on shaking, or can be dissolved in ethyl acetate and precipitated with anhydrous ether ; a confusedly crystalline mass, of a fine yellow colour, is thus obtained. This decomposes sharply at 163° C., and on analysis gives :—$C = 42{\cdot}10$; $H = 5{\cdot}25$; $N = 14{\cdot}35$ per cent. $(C_{10}H_{15}N_3O_7)_2$ requires $C = 41{\cdot}52$; $H = 5{\cdot}23$; $N = 14{\cdot}53$ per cent.

The molecular weight in acetone solution, by the boiling-point method is 516, the calculated figure being 578.

On oxidation with permanganate and with nitric acid this substance behaves in the same way as *nitrosite C*.

It seems, at first sight, that there is no property by which the nitrosite of dimyrcene can be differentiated from the caoutchouc nitrosite.

The residual polymyrcene also yields, with nitrous acid, a nitrosite which resembles in its properties the nitrosite just described, and which crystallises in plates from an ethyl acetate solution. These also decompose at 163° C., and give on analysis :—$C=52{\cdot}83$; $H=6{\cdot}16$; $N=9{\cdot}42$ per cent. $C_{40}H_{56}N_6O_{18}$ requires $C = 52{\cdot}86$; $H = 6{\cdot}16$; $N = 9{\cdot}25$ per cent.

The molecular weight in acetone solution by the boiling point method is 896, the calculated value being 908. When treated exhaustively with nitrous acid, this polymyrcene nitrosite appears to break down into dimyrcene nitrosite according to the equation—

$$C_{40}H_{56}N_6O_{18} + 3N_2O_3 + 2H_2O \rightarrow 2(C_{20}H_{30}N_6O_{14}).$$

The action of nitrous acid upon other terpenes, such as limonene or

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[1] *Ph. Rundschau*, 1895, 13, 60.

[2] *Ber.*, 1901, 34, 3122.

[3] Myrcene belongs to the open chain series ; it is hexavalent. It is a liquid which can be extracted from the myrtles. Its usual form is Essence of Bay. It boils at 67° to 68° C. at 20 mm. ; its density is 0·8203 at 15° C. It is etherified by acetic acid and sulphuric acid. On saponification these ethers yield linalool.

dipentene, preferably after polymerisation by heat, did not result in the formation of any nitrosite comparable with *nitrosite C*.

On the other hand, if the fraction boiling at 31° C. from the dry distillation of Para rubber—a fraction which consists almost entirely of isoprene—be heated at 300° C., it can be polymerised to products greatly resembling di- and polymyrcene. Harries and Wiess treated these bodies with nitrous acid, under conditions similar to those laid down for the formation of nitrosites, and already described, and they obtained similar nitrous compounds, decomposing at about 163° C.

The same result was obtained by the nitrosation of the residue on distillation of rubber, which does not distil at 300° C. under ½ mm. pressure.

Harries rightly says that " this array of facts indicates beyond any doubt a close genetic relationship between myrcene, isoprene, and caoutchouc."

The behaviour of the nitrosites of dimyrcene and polymyrcene, which differ from one another in percentage composition and molecular weight, explains why the action of nitrous acid on pure rubber often gives products differing in these two respects. It may, in fact, be assumed that in presence of moisture the polynitrosite $C_{40}H_{56}N_6O_{18}$ is formed, and that this gradually breaks down under the influence of the prolonged action of nitrous acid, taking up the elements of water and forming two molecules of $C_{20}H_{30}N_3O_{14}$.

On the other hand, the polynitrosites of the form $C_{20}H_{30}N_3O_{14}$ seem to be characteristic of the aliphatic diterpenes, and represent a new type of compound.

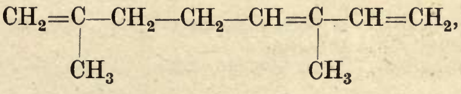
But, it may be asked, if this hypothesis that caoutchouc belongs to the class of open-chain polyterpenes be admitted, how can the presence of dipentene amongst the products of dry distillation be explained ? The answer is simple if the possibility of a secondary reaction be allowed, in which either isoprene first formed undergoes polymerisation, or the structure of the di-isoprene becomes modified. In addition to dipentene, which constitutes about one-third, Harries in fact isolated other $C_{10}H_{16}$ hydrocarbons from the products of dry distillation.

The fraction boiling between 150° and 200° C. yielded on further fractionation, four portions boiling, under 15 to 16 mm. pressure, respectively at 50° to 60° C., 60° to 65° C., 65° to 70° C., and 70° to 80° C. After redistillation of the intermediate fractions three products were obtained, of which dipentene was one, whilst the other two hydrocarbons had the following characteristics :—

Hydrocarbon A, dried over sodium, boiled at 147° to 150° C. at normal pressure ; it is a colourless oil with the following physical constants :— Density at 20° C. = 0·8286 ; optical properties, $n_D^{20\cdot5°} = 1\cdot4962$; molecular refraction = 45·24 (calculated for $C_{10}H_{16}$ with two ethylene linkages = 44·92, with three such linkages = 46·94). Analysis gave C = 87·15 ; H = 12·11 per cent. $C_{10}H_{16}$ requires C = 88·23 ; H = 11·77 per cent.

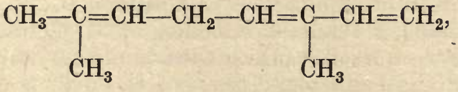
Hydrocarbon B, dried over sodium, boils at about 168° to 169° C. at ordinary pressure. It is a colourless oil with an odour of dipentene, and forms neither a tetrabromide nor a nitrosite, although it is coloured violet by the action of bromine.

Hydrocarbon A is very probably *di-isoprene*,



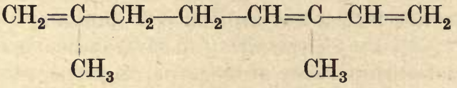
$$CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}CH_2{-}CH_2{-}CH{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}CH{=}CH_2,$$

which is very closely related to *myrcene*,



$$CH_3-\underset{\substack{| \\ CH_3}}{C}=CH-CH_2-CH=\underset{\substack{| \\ CH_3}}{C}-CH=CH_2,$$

and it may be supposed that caoutchouc is derived from it by the condensation of a certain number of molecules, each exchanging one double bond for a neighbouring molecule, or group. The fundamental molecule of caoutchouc, $C_{10}H_{16}$, would then be di-isoprene—



$$CH_2=\underset{\substack{| \\ CH_3}}{C}-CH_2-CH_2-CH=\underset{\substack{| \\ CH_3}}{C}-CH=CH_2$$

and caoutchouc, formed by the polymerisation of an unknown number of molecules of di-isoprene, would be an open-chain hydrocarbon with three double bonds—which is a very doubtful supposition. These conclusions are rendered still more open to discussion by the results obtained by Alexander—which differ from those of Harries—on allowing nitrous acid to act on rubber; Alexander's results indicate the formation of a nitrosite, $C_9H_{12}N_2O_6$.

The very foundation underlying Harries' opinion, from the point of view of the constitution of caoutchouc, consists in the perfect analogy between *nitrosite C* and the nitrosites of myrcene. But it seems to follow from Alexander's results—which the work of Gottlob[1] and Korneck,[2] Harries' pupils, has not entirely refuted—that the products obtained by the action of nitrous acid on rubber are not completely homogeneous.

Also, it is understood that Harries' first opinion underwent some change, and in his lecture at Dantzig[3] he was led to make the following statement:—"I thought caoutchouc was a derivative of the aliphatic terpenes, an open-chain hydrocarbon. I was confirmed in this opinion when I obtained, by the action of nitrous acid on dimrycene, a nitrosite quite analogous with the *nitrosite C* of rubber. It was, however, recognised later that the nitrosites of caoutchouc and dimyrcene, although analogous, are not identical, and up to now it has not been found possible to adduce rigorous proof of the homogeneity of *nitrosite C*." The formation of carbon dioxide, pointed out by Alexander, and confirmed by Gottlob, who attributes it to a secondary reaction, shows that oxidation of CH_3 groups and formation of an unstable carboxyl group must take place, the latter being easily split off from the molecule by heat, liberating carbon dioxide, a change which does not occur in the nitrosation of myrcene. Under these circumstances it cannot be held that the nitrosites are identical, and that their structural formulæ are analogous. The problem had reached this stage when the study of the ozonides of rubber, by Harries and his students, enabled a solution to be found.

We have already explained that when ozone reacts with caoutchouc the latter is depolymerised, and split up into its fundamental molecules. We have shown that the formation of a diozonide clearly demonstrates the presence of two ethylene linkages in the $C_{10}H_{16}$ molecule, and we have

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[1] Lecture at Kiel, 1908, *Zeit. angew. Chem.*, 1907, 20, 2213.
[2] *Gummi Zeit.*, 1910, 25, 77.
[3] *Zeit. angew. Chem.*, 1907, 20, 1265.

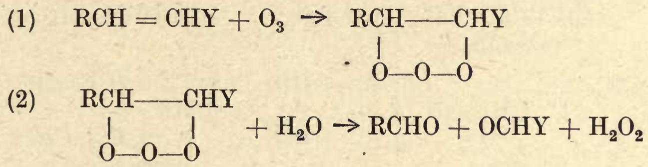
also stated that by the action of boiling water the ozonide is converted into levulinic aldehyde, hydrogen peroxide being also formed, according to the equation—

$$C_{10}H_{16}O_6 + H_2O = [CH_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CHO]_2 + H_2O_2.$$

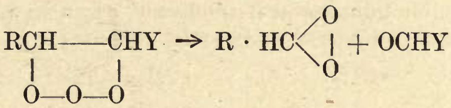
The hydrogen peroxide then reacting with the levulinic aldehyde, partially oxidises it to levulinic acid. In reality the reaction is much less simple.

In his communication to the *British Association at York, in* 1907, Harries said :—" The ozonides are converted, on contact with water, into aldehydes, the scission always occurring at the double bond."

The general course of the reaction is as follows :—



but under certain circumstances peroxides may be formed—

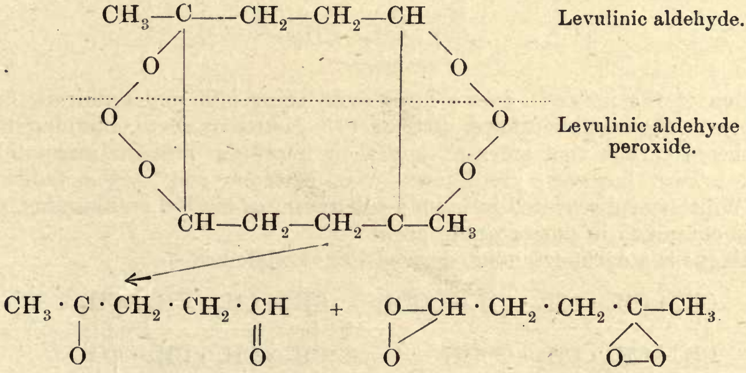


From the ozonide of caoutchouc, therefore, the following products may be obtained :—

(1) Levulinic aldehyde.
(2) Levulinic peroxide or diperoxide.
(3) Levulinic acid.

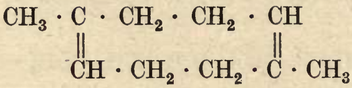
$$CH_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CHO + H_2O_2 \rightarrow CH_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot COOH + H_2O.$$

It follows that caoutchouc ozonide must contain a cyclic nucleus with an 8-carbon ring, which splits up at the two double bonds into levulinic aldehyde, and levulinic diperoxide ; this is indicated by the dotted line in the following formula—



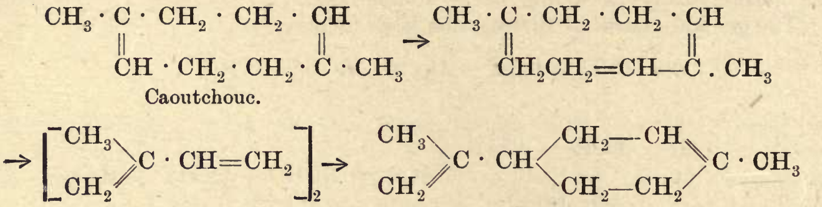
Levulinic aldehyde. Levulinic aldehyde peroxide.

The original hydrocarbon, $C_{10}H_{16}$, must, therefore, have the following constitution :—



$$\begin{array}{l} CH_3 \cdot C \cdot CH_2 \cdot CH_2 \cdot CH \\ \qquad \| \qquad\qquad\qquad\qquad \| \\ \qquad CH \cdot CH_2 \cdot CH_2 \cdot C \cdot CH_3 \end{array}$$

which is that of a 1·5 dimethy-l*cyclo*-octadiene 1·5. This constitutional formula is in accordance with the possibility of splitting the $C_{10}H_{16}$ molecule into isoprene, and with the formation of dipentene, under the influence of heat. Thus—

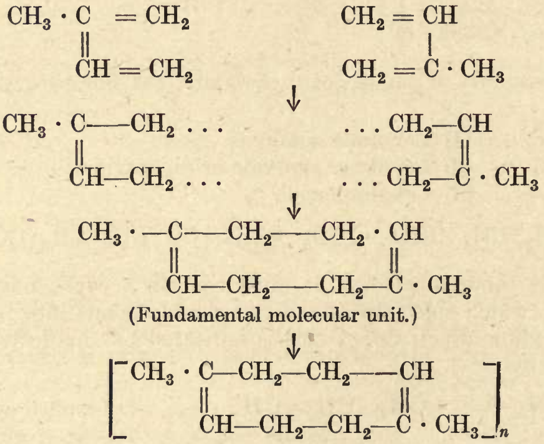


Caoutchouc.

Isoprene.

Dipentene.

The synthesis of caoutchouc, starting with isoprene, a hydrocarbon containing conjugate double linkages in its molecule, can also be readily understood with the aid of Thiele's theory of partial valencies :—



$$\begin{array}{ll} CH_3 \cdot C = CH_2 & CH_2 = CH \\ \quad \| & \qquad\quad | \\ \quad CH = CH_2 & CH_2 = C \cdot CH_3 \end{array}$$

$$\downarrow$$

$$\begin{array}{ll} CH_3 \cdot C — CH_2 \ldots & \ldots CH_2 — CH \\ \quad \| & \qquad\qquad \| \\ \quad CH — CH_2 \ldots & \ldots CH_2 — C \cdot CH_3 \end{array}$$

$$\downarrow$$

$$\begin{array}{l} CH_3 \cdot — C — CH_2 — CH_2 \cdot CH \\ \qquad\quad \| \qquad\qquad\qquad\quad \| \\ \qquad\quad CH — CH_2 — CH_2 — C \cdot CH_3 \end{array}$$

(Fundamental molecular unit.)

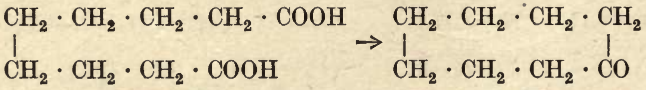
$$\downarrow$$

$$\left[\begin{array}{l} CH_3 \cdot C — CH_2 — CH_2 — CH \\ \qquad\quad \| \qquad\qquad\qquad\quad \| \\ \qquad\quad CH — CH_2 — CH_2 — C \cdot CH_3 \end{array}\right]_n$$

Caoutchouc.

the value of the index *n*, as we have seen, being still undetermined, but probably in the neighbourhood of 8 or 10. Hydrocarbons containing the 8-membered carbon ring are rare, and their formation presents great difficulties. Two, however, are known—viz., azelaone and cyclo-octadiene, which Willstätter discovered in pseudo-pelletierin, or methyl granatonine, an alkaloid contained in pomegranate peel.

Azelaone is a cyclo-octanone, derived from azelaic acid—



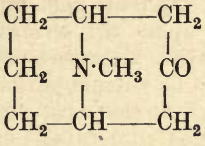
$$\begin{array}{l} CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot COOH \\ | \\ CH_2 \cdot CH_2 \cdot CH_2 \cdot COOH \end{array} \rightarrow \begin{array}{l} CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \\ | \qquad\qquad\qquad\qquad\quad | \\ CH_2 \cdot CH_2 \cdot CH_2 \cdot CO \end{array}$$

Azelaic acid. Azelaone (cyclo-octanone).

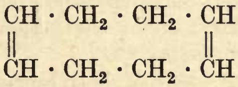
The process by which it is produced is an application of the principle of Wislicenus, according to which cyclic ketones can be obtained by heating the calcium salts of adipic acid or alkyl-adipic acids, to which latter category azelaic acid belongs.

According to Dale and Schorlemmer,[1] azelaone is a homologue of suberone.

Pseudo-pelletierin or methyl granatonine, $C_9H_{15}NO$, is a ketone with a very strongly basic reaction, and the following structural formula :—



From this ketone Willstätter's hydrocarbon can be obtained. This has the following structure :—



in which, as in the caoutchouc formula, two ethylene linkages in the 1·5 position are present. On ozonisation, followed by hydrolysis with water, it yields succinic dialdehyde—

$$CHO \cdot CH_2 \cdot CH_2 \cdot CHO$$
$$CHO \cdot CH_2 \cdot CH_2 \cdot CHO$$

Cyclo-octadiene undergoes polymerisation when heated at about 70° C., yielding, under certain conditions, a product which bears a very strong resemblance to rubber.

The action of ozone on guttapercha, which is an isomeride of caoutchouc, yields an ozonide which, when decomposed by water, forms the same products as the ozonide of caoutchouc—viz., aldehydes, levulinic peroxide, and levulinic acid—but in different proportions.

All the experiments made with a view to reducing caoutchouc ozonide and thus to preparing (unpolymerised) dimethyl-*cyclo*-octadiene have so far failed, and Harries confesses that he has not been able to synthesise this compound, which, therefore, still remains unknown.

The parent hydrocarbon of caoutchouc being this dimethyl-*cyclo*-octadiene, the questions arise as to what is its degree of polymerisation? Under what influences does polymerisation take place? How are these molecules grouped to form the larger complex, and do they form a cyclic or an open-chain complex?

On these points investigation is not so well advanced; discussion as to the way in which the fundamental molecules, $C_{10}H_{16}$, are linked up, is still perfectly free, whilst English and German theories on the subject are in conflict. It is only known that the links are very weak, since bromine, iodine, nitrous acid and ozone readily snap them, liberating the units $C_{10}H_{16}$. As to the number of the latter in the caoutchouc molecule, this cannot yet be fixed with any degree of certainty.

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[1] *Ber.*, 1879, 12, 2383.

Kondakow[1] has put forward a complete theory of polymerisation, which is on very similar lines to that of Victor Henri on coagulation. He maintains, in effect, that the faculty of polymerisation of fundamental groupings, $C_{10}H_{16}$, is dependent upon the electro-negative groups which they contain. In particular, he explains the tendency to polymerise shown by compounds of the divinyl series by the presence in ethylene and ethylenic hydrocarbons, of a new unsaturated radicle, with electro-negative properties.

"The essential cause of the faculty observed to belong to hydrocarbons of the divinyl-group—viz., that of undergoing polymerisation—depends to a considerable extent upon the electro-negative properties of the molecule of these unsaturated hydrocarbons. In the second place, it depends upon the conditions of polymerisation, for all the data brought forward, which were selected as the most typical out of a large number, entirely confirm the proposition enunciated—viz., that ethylene derivatives, formed by substitution of electro-negative elements or groups for hydrogen atoms, exhibit a very special tendency to polymerise under the influence of light (photopolymerisation), heat (pyropolymerisation), or spontaneously (autopolymerisation), or, lastly, under the influence of acids, alkalies, salts, and metals (polymerisation by catalysis)."

"Since, according to the ideas of Marckwald,[2] Heinrich,[3] Charon,[4] and Thiele,[5] the double bond possesses electro-negative properties, it is conceivable that substitution products of ethylene itself, containing such unsaturated electro-negative radicles, will be as ready to polymerise as any of the previously mentioned compounds."

"Actually, it is found that di-isopropenyl or dimethyl, 2·3 butadiene :—

$$CH_2 = C(CH_3) \cdot C(CH_3) = CH_2$$

does polymerise under the influence of light, or of alcoholic potash, that the same is true of isoprene and butadiene, and that consequently it must be the same with various other substitution products of this hydrocarbon." Kondakow, nevertheless, believes that polymerisation by light gives hydrocarbons of greater complexity than the other processes, and that this would explain the value of natural rubber.

Molecular weight determinations would give some information on this point, but, unfortunately, scarcely anything is known on the subject.

It is admitted, in a general way, that colloids are characterised by enormously high molecular weights, and various chemists—Pfeffer, Linebarger, Sabanejew, Alexandrow, Vaubel, Gladstone, and Hibbert—who attempted to make determinations, obtained some extraordinary results. For caoutchouc Gladstone gives the figure 6,504 ; Hinrichsen and Kindscher, using the Beckmann freezing-point method, in benzene found the value 3,713 ; these values give to n a value between 27 and 47.

"Only a very relative value must be attached to these figures," says Weber, "for they relate to molecular complexes which are in a continuous state of change, depending on the nature and condition of the solvent. The determination of the molecular weight of rubber is an operation of extreme difficulty on account of the viscosity even of dilute solutions. The boiling point method cannot be used, because, as soon as heat is applied to such

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[1] *Actes de la faculté de Dorpat*, 1901, No. 1, p. 7.

[2] *Ber.*, 1895, 28, 1501.

[3] *Ber.*, 1898, 31, 2103.

[4] *Comptes rend.*, 1899, 128, 736.

[5] *Ber.*, 1900, 33, 668

solutions, they no longer remain homogeneous, coagulated pellicles forming at the heated surface."

Even if a result were obtained in this way the figure would not be reliable, for in presence of solvents it is almost certain that rubber is depolymerised.[1] Under these circumstances it is easy to understand why better results have not been obtained with the derivatives—chlorides, bromides, iodides, nitrosites, phenolic compounds.

On the other hand, the cryoscopic method is no more applicable than the osmotic method. On account of their very feeble osmotic pressure, colloids, as Pfeffer has shown, have exceedingly little influence upon the freezing point of their solvents.

The nearest molecular weight is evidently that obtained by Hinrichsen and Kindscher,[2] who employed the cryoscopic, whereas Gladstone and Hibbert used the ebullioscopic method.

Hinrichsen and Kindscher, who, contrary to Weber's views, hold that rubber pre-exists in the latex, and that its separation is due to physical phenomena, employed *Kickxia* latex to determine the molecular weight.

The latex was extracted with benzene at ordinary temperatures, and, by afterwards centrifuging and filtering, a limpid colloidal solution was obtained; with this a molecular weight determination was made in the Beckmann apparatus, the concentration of the solution being found by evaporation to dryness. A correction was made for the resins present by exhaustively extracting these from the residue on evaporation by means of acetone, recovering them by evaporation to dryness, and carrying out with them a fresh Beckmann determination. From the difference between the two values the molecular weight of the caoutchouc was calculated, and was found to be, as we have already stated, 3,173. This value is a lower limit, for the caoutchouc is certainly accompanied by substances which are soluble in benzene and insoluble in acetone, and which have an effect on the depression of the freezing point.

In spite of the meticulous precautions adopted by Hinrichsen and Kindscher, and of the care with which their investigation was carried out, Weber's reservations lose nothing of their value, and it is unlikely that the figure obtained is the true value.

Despairing of getting a direct result, attempts have been made to gather some information from the phenomena of vulcanisation, which, if it did not give an exact value, might at least give some idea of the size of the polyprene molecule, and the value of the index n.

On referring to the theory of vulcanisation formulated by Weber,[3] it will be seen that the latter regards this phenomenon as a process of *pectisation* brought about by chemical influences, and that he looks upon the fixation of sulphur by rubber as an additive reaction.

On the other hand, it is found that in vulcanisation it is not, as in bromination or nitrosation, the fundamental $C_{10}H_{16}$ molecule which comes into play, but rather the complete polyterpene $(C_{10}H_{16})_n$; since no depolymerisation occurs a series of sulphuretted compounds is possible from $(C_{10}H_{16})_n S$ to $(C_{10}H_{16})_n S_{2n}$, which would represent a saturated compound.

If, then, a given weight of rubber be vulcanised with a large excess of

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[1] Its solubility in solvents must, moreover, be a function of its degree of polymerisation, which explains why one author finds it soluble and another insoluble in ether.

[2] *Ber.*, 1909, 42, 4329.

[3] *Gummi Zeit.*, 1902, 17, 528-561.

sulphur, and the uncombined sulphur be afterwards extracted with acetone, it will be possible to ascertain by analysis the amount of sulphur which has been fixed, and to calculate from this how many $C_{10}H_{16}$ molecules have come into play, and consequently the composition of the polyprene molecule.

This limit of vulcanisation was found by Weber to correspond with a compound $C_{100}H_{160}S_2$. Since it requires S_2 to saturate the single group $C_{10}H_{16}$, the conclusion may be drawn that the caoutchouc complex may be represented by $(C_{10}H_{16})_{10}$, the index n being equal to 10; unless, as is rather unlikely in cold vulcanisation at any rate, superpolymerisation has taken place.

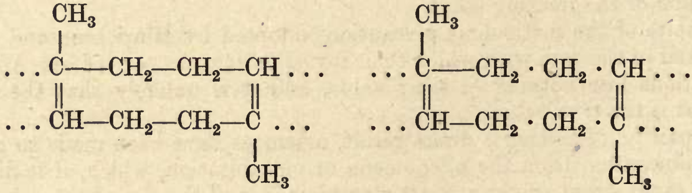
This result is obviously very hypothetical, so much the more as Ostwald[1] now maintains that in vulcanisation, contrary to Weber's opinion, chemical combination between rubber and sulphur does not occur, but only physical adsorption, as in the case of textile fabrics and dyestuffs.

This theory, although it has been disputed by Alexander, appears to be of considerable weight, and the authority of its sponsor renders it worthy of very careful consideration. Nevertheless, certain facts, such as reversibility in hot vulcanisation, and the presence of sulphur in the nitrosites and tetrabromides, derived from vulcanised rubber, add weight to the theory of chemical combination.

However that may be—and the examination of this problem does not come within the scope of our study—it will be seen how uncertain is the information as to the molecular weight of $(C_{10}H_{16})_n$ to be derived from the phenomenon of vulcanisation.

The structure of the fundamental molecule is, then, definitely established; that of the caoutchouc complex is less clearly defined.

Harries, like Lebedeff, supposes that, in order to form the complex, a number of molecules of dimethyl-*cyclo*-octadiene becomes linked up by means of the partial valencies, in accordance with the ideas of Thiele :—



$$\begin{array}{llll} & \mathrm{CH_3} & & \\ & | & & \\ \ldots & \mathrm{C—CH_2—CH_2—CH} & \ldots & \\ & \| \qquad\qquad\qquad \| & & \\ \ldots & \mathrm{CH—CH_2—CH_2—C} & \ldots & \\ & \qquad\qquad\qquad\quad | & & \\ & \qquad\qquad\qquad \mathrm{CH_3} & & \end{array} \qquad \begin{array}{llll} & \mathrm{CH_3} & & \\ & | & & \\ \ldots & \mathrm{C—CH_2 \cdot CH_2 \cdot CH} & \ldots & \\ & \| \qquad\qquad\qquad \| & & \\ \ldots & \mathrm{CH—CH_2 \cdot CH_2 \cdot C} & \ldots & \\ & \qquad\qquad\qquad\quad | & & \\ & \qquad\qquad\qquad \mathrm{CH_3} & & \end{array}$$

It will be seen at once that this kind of polymerisation may give rise to a considerable number of isomerides; and the idea may be utilised in order to explain the existence of the numerous varieties of rubber.

In order to explain the action of ozone, and the formation of the diozonide, and levulinic aldehyde, it is sufficient to assume that the complex is first of all depolymerised by the ozone, before the latter acts upon the $C_{10}H_{16}$ group.

This theory is now accepted by German and Russian chemists, but is contested by English chemists, from Weber to Pickles; these latter regard the complex as formed by the chemical union of C_5H_8 or $C_{10}H_{16}$ groups to form a long open chain.

Harries' hypothesis derives support from a recent observation made in connection with the synthetic rubber derived from butadiene—

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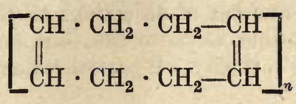
[1] *Zeit. Chem. Ind. Koll.*, 1910, 6, 135.



The ozonide of this rubber is identical with that of the *cyclo*-octadiene, 1·5 obtained by Willstätter from pseudo-pelletierin[1]; on decomposition by water these two ozonides yield the same quantity of succinic aldehyde.

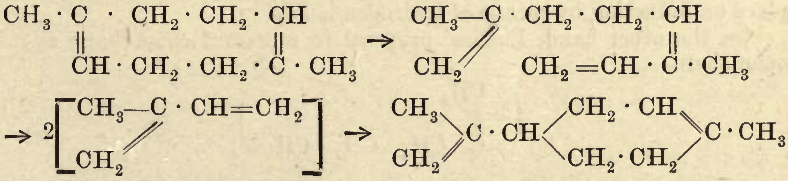
Nevertheless, it is to be noted that the ozonides are not the same in appearance[2]; the ozonide of *cyclo*-octadiene is a white powder, highly explosive, hydrolysed with difficulty by water, and yielding no H_2O_2; the ozonide of butadiene rubber is, according to the solvent employed, either an oil with an H_2O_2 reaction and hydrolysing readily, or a solid which does not give the H_2O_2 reaction.

Harries' hypothesis enables an explanation to be given of the remarkable similarity between the ozonides of guttapercha and rubber, for these two substances are both polymerides, of different degrees of complexity, of the same fundamental hydrocarbon; the difference between them is merely in the size of their molecules.

The facts which must be explained by any constitutional formula for caoutchouc have been set out by Barrow, as follows :—

1. The formation, by interaction with ozone, of an ozonide, resulting from the direct addition of O_3 to a depolymerisation product.
2. The formation of an additive tetrabromide, by interaction with bromine.
3. The production, not of a *cyclo*-octadiene, but of a dipentene—containing a six-carbon ring—when rubber is depolymerised by heating it with a solvent of high boiling point.
4. The production of a series of decomposition products when rubber is subjected to dry distillation.
5. The conversion of caoutchouc into a saturated hydrocarbon by reduction with hydrogen.
6. The formation of caoutchouc by polymerisation of isoprene, but not of dipentene.
7. The spontaneous "super"-polymerisation of rubber on keeping, and the reversibility of this process.
8. The sufficiency of small quantities of sulphur to bring about complete vulcanisation.

It is only necessary to examine Harries' formula to see that it fulfils all these conditions; the only point about which discussion might arise is the formation of dipentene, but if opening of the C_8 ring be assumed to occur under the influence of heat, Barrow's postulate is completely satisfied, as in the following scheme :—



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[1] *Ber.*, 1905, 38, 1975; 1907, 40, 957.

[2] Harries, *Annalen*, 1911, 383, 157; 1911, 385.

Pickles has raised a number of objections to Harries' formula, which he almost regards as impossible, because the German chemist is compelled to have recourse to Thiele's theory of partial valencies, in order to explain polymerisation.

On this explanation, he says, it would be expected that the polymerisation would be of a purely physical character, or that the link between the molecules would be very weak; but this does not agree with the behaviour of the derivatives of rubber.

It would be necessary to assume that all substances which react with caoutchouc, from bromine to ozone, first of all bring about depolymerisation before combining with it.

If polymerisation were purely physical in chacacter one should obtain, on distillation *in vacuo*, the fundamental molecule—that is to say, the hydrocarbon with the smallest number of carbon atoms; but actually compounds containing 20 atoms of carbon are obtained.

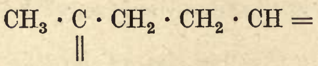
The reduction product of caoutchouc should, according to Harries' formula, be a terpene boiling at 170° C., whereas, on reducing caoutchouc with hydrogen iodide, Berthelot obtained paraffinoid hydrocarbons, boiling at about 350° C.

If caoutchouc were produced by the polymerisation of 8-carbon rings, it should, when treated with bromine, either remain polymerised and add on only two atoms of bromine, or it should become depolymerised and add on four atoms; in actual fact it remains polymerised and adds on four atoms.

If the hypothesis of an open-chain structure be admitted, polymerisation can be viewed as a phenomenon of a purely chemical order. The action of ozone can then be more easily explained; acting at the double bonds it would separate two carbon atoms—

$$C = C + O_3 \rightarrow C—O—O—O—C.$$

In conclusion, Pickles proposed for caoutchouc a nucleus with a much greater number of carbon atoms, corresponding with the molecular weight; the differences observed between the various sorts of rubber would then be explained by the number of

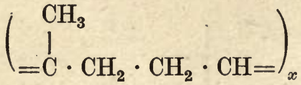


$$CH_3 \cdot \underset{\|}{C} \cdot CH_2 \cdot CH_2 \cdot CH =$$

groups in the chain.

In replying to the criticism of Pickles, Harries complained that he had brought forward no experimental data in support of his arguments; moreover, Berthelot's observation on the reduction of caoutchouc cannot be taken as evidence, because of the molecular rearrangement which always takes place on reduction by means of hydrogen iodide.

On the other hand, Pickles' proposal to represent caoutchouc as a long open chain—



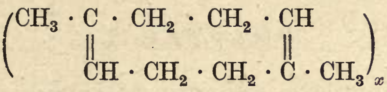
$$\left(= \overset{\displaystyle CH_3}{\overset{|}{C}} \cdot CH_2 \cdot CH_2 \cdot CH = \right)_x$$

containing at least eight of the above links, hardly satisfies the mind; with its aid it is difficult to explain the phenomena of polymerisation and depolymerisation, and still more difficult to explain those of vulcanisation.

Weber showed that from 2 to 2·5 per cent. of sulphur is sufficient for complete vulcanisation, and it is difficult to imagine how this small absorption of sulphur by Pickles' long chain can explain the fact. Under these circumstances the majority of chemists support Harries' formula, which is almost universally accepted.

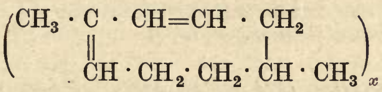
It only applies to the constitution of natural rubber; in the case of the synthetic rubber, which we shall study shortly, even in the case of isoprene rubber, since more than one product is obtained, the formula must be modified by altering the position of certain double bonds.

The greater part of the synthetic product has the constitution of natural caoutchouc—



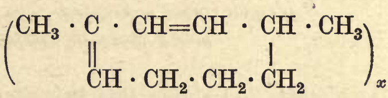
$$\left(\begin{array}{llllll} \mathrm{CH_3}\cdot & \mathrm{C} & \cdot\,\mathrm{CH_2}\,\cdot & \mathrm{CH_2}\,\cdot & \mathrm{CH} & \\ & \| & & & \| & \\ & \mathrm{CH} & \cdot\,\mathrm{CH_2}\,\cdot & \mathrm{CH_2}\,\cdot & \mathrm{C} & \cdot\,\mathrm{CH_3} \end{array}\right)_x$$

the other portions having the isomeric constitution—



$$\left(\begin{array}{lllll} \mathrm{CH_3}\cdot & \mathrm{C} & \cdot\,\mathrm{CH{=}CH}\,\cdot & \mathrm{CH_2} & \\ & \| & & | & \\ & \mathrm{CH} & \cdot\,\mathrm{CH_2}\cdot\mathrm{CH_2}\cdot & \mathrm{CH} & \cdot\,\mathrm{CH_3} \end{array}\right)_x$$

or



$$\left(\begin{array}{lllll} \mathrm{CH_3}\cdot & \mathrm{C} & \cdot\,\mathrm{CH{=}CH}\,\cdot & \mathrm{CH} & \cdot\,\mathrm{CH_3} \\ & \| & & | & \\ & \mathrm{CH} & \cdot\,\mathrm{CH_2}\cdot\mathrm{CH_2}\cdot & \mathrm{CH_2} & \end{array}\right)_x$$

The ozonides of these two rubbers yield decomposition products other than levulinic aldehyde or levulinic acid, such as methylglyoxal, or pyruvic aldehyde.

This, of course, does not militate in any way against Harries' theory; on the contrary, it indicates the value of the constitutional formula suggested by him, in that it affords an explanation of all the observed facts.

SECTION III.

THE SYNTHESIS OF CAOUTCHOUC.

CHAPTER XI.

ISOPRENE AND ITS HOMOLOGUES.

> "*L'esprit étonné se demande, non pas à quoi on emploi le caoutchouc, mais bien à quoi cette substance n'a pas été encore utilisée.*"

The truth underlying this shrewd observation of Aimé Girard is at once an indication of the importance of this wonderful product and an earnest of the unlimited uses to which it could be put if, whilst preserving its valuable properties intact, it could only be produced at lower cost.

To the question, whether the solution of this problem lies in the direction of chemical synthesis, we would reply in the affirmative.

We believe firmly that the future of rubber lies in its synthetic production ; not in the embryonic processes of which we now have cognisance, but, of course, in a synthesis put on a proper industrial basis. Nevertheless, with Harries it must be admitted that, in spite of the fine speculations of Ditmar, who has visions of Germany as the sole producer of rubber, we have not yet arrived at that point—far from it.

When we come to look into what has already been done and consider what remains to do, the distance separating cup and lip, dream and reality, becomes very apparent.

To use a metaphor, we have before us some extremely beautiful laboratory blossoms, but we are entirely in the dark as to whether these will develop into the delicious fruits of industry.

Both natural and synthetic production have one aim in common, and that is to obtain a material which, although it is a *chemical compound* with a known fundamental molecule—yet of an unknown degree of polymerisation—must respond to *mechanical strain* in a way that can only be compared to the behaviour of living muscle—an analogy, the boldness of which is not only excusable but quite justified in the light of Chauveau's masterly investigations.

This idea has, indeed, received a very general interpretation in a literal sense, and the view has been held that the synthesis of caoutchouc is not possible, because living matter is being dealt with. From Gerber to Vernet, the same feeling has existed amongst men who know rubber not only from a scientific but also from a practical standpoint.

And there is a certain amount of truth in the aphorism, because, if we refer to the interesting results of the work of Bouasse, Breuil, Boutaric, and others, we find that rubber possesses some singular properties, which stamp it with a quite unique chemical individuality.

What is the origin of these properties if not the state of polymerisation? For as this state varies the elasticity and tensile strength of the rubber increase or diminish.

It is quite evident that there is a close connection between the structure of caoutchouc and its mechanical properties, and the structure is dependent upon two things: (1) the state of polymerisation of the fundamental hydrocarbon, represented by the complex $(C_{10}H_{16})_n$; (2) the arrangement of these polymeric molecules into the physical grouping ("colloidal aggregate," Schidrowitz), known as commercial rubber.

Now about polymerisation we know practically nothing, and yet it is there that the whole secret of a complete synthesis lies.[1]

Just as in the case of natural rubber the one operation of prime importance is the process of coagulation, so in the case of the synthetic product the one great problem is to be able to effect a condensation of the primary products of synthesis in such a way that the condensed or polymerised product is mathematically identical with natural caoutchouc.

It must never be forgotten that we are dealing with a colloidal complex, and that, therefore, the data of the problem are of quite another order than those which exist in the case of the indigo and camphor syntheses, with which a comparison is too often drawn. In each of these two cases it was only necessary to reproduce a crystalloid, admittedly a difficult problem, but one in which all the unknowns had been determined. In the case of caoutchouc it is nothing to obtain the fundamental hydrocarbon; it is the complete complex which must be re-formed, and we do not even know what the size of this complex is. Nevertheless, upon the way in which it is made up the whole of the characteristic properties of caoutchouc depend.

There is one thing which strikes one, when examining all the known facts relative to the synthesis—namely, the absence of a broad outlook, of a philosophic spirit, in the conduct of the researches on the subject. By plunging into minute analytical details the structure of the fundamental hydrocarbon has been determined; then, as the result of patient effort, it has been raised to various degrees of polymerisation, which make of the synthetic products obtained only isomers of the natural product, for it has never been shown by means of a series of mechanical tests—which are the only tests that count so far as the complex is concerned—that these products are identical with natural caoutchouc, and possessed of all its properties.

In the case of a body with such peculiar properties as rubber, chemical analysis is, in spite of Harries' contention, powerless to afford means of identification which shall be beyond cavil. For whatever may be the rubber-like material obtained, if it only contain the $C_{10}H_{16}$ group in the form of the dimethyl-*cyclo*-octadiene nucleus, no matter what the degree of polymerisation, it will always yield, by interaction with ozone followed by hydrolysis, the levulinic derivatives isolated by Harries. The complex will first of all be depolymerised, and the chemical reaction will ensue. Thus the formation of levulinic aldehyde cannot in any sense be taken as a proof that we are

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[1] Harries said in his lecture in Vienna—"We know nothing definite about the size of its molecule; naturally we have no knowledge of the relationships which exist between the different modifications; we do not even know whether we are dealing with a form of physical polymorphism, as in the case of sulphur, or with polymerism."

dealing with a true caoutchouc, but merely that the substance in question is a polymeride of dimethyl-*cyclo*-octadiene, obtained by some happy chance. It will demonstrate analogy, but not identity.

This importance of polymerisation, its mechanism, its degree, which are the determining causes of the physical properties, and, therefore, of the technical value of rubber, seems somewhat to have escaped the notice of the German chemists.

On referring to everything that has been written about the synthesis, and looking through the extensive patent literature on the subject, one is astounded at the vagueness and lack of precision in all the details relating to polymerisation. The particulars given of the temperatures to be employed and of the duration of heating vary *ad infinitum.* The impression conveyed is that of an empirical rather than a scientific solution of the problem.

In this connection Harries, who is as a rule very clear, becomes almost obscure; Kondakow, despite his wordiness and his prolixity, remains nebulous; Duisberg alone is definite. So long as we do not know with certainty the number and arrangement of the fundamental units in the complex, so long as we do not possess the secret of the polymerisation of caoutchouc, so long will it be a very difficult matter to produce the substance at will, and the problem of synthesis will remain almost untouched.

But now, supposing for a moment that these difficulties were all removed, and that this part of the problem were completely solved, would the realisation of the industrial synthesis follow? That is still open to discussion.

From the manufacturing point of view a chemical synthesis is devoid of interest until it is possible to produce the substance in question at a price lower than that which it costs to extract it from natural products. If the cost of the synthetic product is the higher, then in spite of all the elegance of the process, and the ingenuity displayed in it, the effort will be wasted and the synthesis will remain without interest.

But it will be remembered that we showed that plantation rubber costs about 1s. 1½d. per lb. to produce; the synthetic product must, therefore, be capable of production below this figure. From what we are, at the moment, able to learn about the synthesis, the various processes which we shall examine in detail, and the raw materials used, it seems very clear to a chemist familiar with synthetic industry that the cost of the new rubber must far and away exceed that of the natural product, and that if we had to rely upon the known facts, the industrialisation of the process would be almost impossible.

Amongst the proposed methods, however, there are some which merit attention, because hope may be entertained of their further development.

It should not be forgotten that, in organic chemistry, chemical reactions are never realised quantitatively; one has to do with systems in equilibrium, and, therefore, never more than a certain percentage of the desired substance can be obtained. It follows that the fewer the stages in the reaction the more efficient will be the process. On the other hand, the use of certain reagents is very costly, and risks of loss, through volatilisation and on account of the difficulty of recovery, must be taken into consideration in selecting a method. Any process in which iodine, bromine, methyl chloride, or hydrogen gas are used must be regarded as difficult, because the employment of reagents costing from 2s. 6d. to 4s. 6d. per lb. to obtain a product worth from 11d. to 1s. 1½d. is an adventurous operation. The employment of relatively high, constant temperatures is also surrounded with difficulties. Although it is quite possible in the laboratory to maintain a constant temperature of 400° C. by means of a sulphur bath, it is not so simple on the industrial scale. So long as the temperature does not exceed 350° C., as is common in the colour industry and in the synthesis of camphor, it can be obtained quite conveniently by means of an oil bath, but if it be necessary to maintain a temperature of 600° C., as in certain reactions suggested by Harries, thermal regularity is exceedingly difficult to achieve, even though fusible metal baths be employed.

For these purely technical reasons all syntheses which are based upon bromination or methylation, or upon reactions carried out at a high constant temperature seem doomed to failure from an economic point of view. The same remark applies to processes which start with comparatively scarce materials, the price of which is of necessity too high to permit of a manufactured product being turned out at a really remunerative price.

The one thing which has made the success of the colour industry is that the necessary raw material for all the synthetic processes of which it is built up can be obtained in abundance, and at a low cost, from the coal-tar distillates.

Save for a few rare exceptions, such as the use of phenol or cresol, acetylene or petroleum spirit, according to what we know to-day, this state of affairs does not exist in the case of synthetic rubber. Yet if one considers the formation of caoutchouc in the plant, it would seem that the raw materials in this case must naturally be found amongst the very abundant naturally-occurring substances, which cost very little, such as starch, sugar, cellulose, etc., substances which result, as does caoutchouc itself, from the life activity of the plant.

With the reservations which have just been formulated, we propose to set down the present state of our knowledge of the synthesis of caoutchouc as gathered from the work in turn of Bouchardat, Tilden, Kondakow, Harries, Heinemann, Hoffman and Coutelle, the Badische chemists, Perkin, Strange, Graham, Matthews, and Fernbach.

When the news got abroad that, in principle, the synthesis of rubber had been effected, technical circles remained very sceptical. Maclaren in the *India Rubber Journal*, gave a humorous skit describing the conversion of Cheshire cheese into *fine Para*, thanks to the genius of a German chemist, and the serious *India Rubber World* gave the following fantastic recipe for its preparation :—

"Take 10 lbs. of *Para*, 1 gallon of benzole, and 1 oz. of pyrrol; mix thoroughly and allow the solution to evaporate ; then add to 15 parts of the above solution 10 parts of ignorance, 25 parts of avarice, 50 parts of bad faith, the whole mixed in secret, and you will have synthetic rubber."

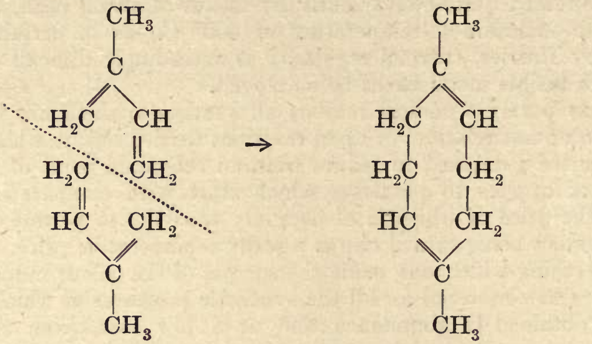
After Harries' lecture at Vienna on March 12th, 1910, in which he explained the then position of research on this subject, the investigations carried out were taken into very serious consideration, and although it was recognised that the methods put forward were not practicable on the commercial scale, this did not detract from their high scientific interest.

Natural rubber being derived from isoprene

$$CH_2 : C(CH_3) \cdot CH : CH_2$$

it followed that caoutchouc, for the fundamental hydrocarbon of which Harries had given a formula, should be obtainable according to the syntheses of Bouchardat and Tilden, matters of chance though these were, despite the fact that Harries and Klages had made unsuccessful attempts to repeat them.

The change would be represented as follows :—



2 molecules of isoprene → 1·5 dimethyl-cyclo-octadiene.

Therefore, by polymerisation of the hydrocarbon C_5H_8 it is possible to obtain a synthetic caoutchouc identical with the natural product, and the only doubt is with regard to the number n of fundamental molecules $C_{10}H_{16}$, in the polymerised complex $(C_{10}H_{16})_n$.

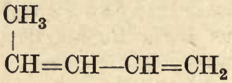
There are lower and higher homologues of isoprene, and it appeared certain that, on polymerising these, new caoutchoucs, having no counterpart in nature, would be obtained.

The first hydrocarbon of the series is *erythrene*, or 1·3 butadiene, or divinyl—

$$CH_2 : CH \cdot CH : CH_2.$$

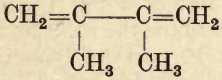
It is upon the system C : C · C : C that the process of polymerisation operates, and it follows that all hydrocarbons which contain this grouping are capable of yielding compounds analogous to caoutchouc; such are the alkyl derivatives of butadiene, as, for example—

Piperylene, ...



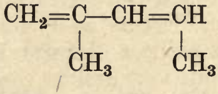
$$\overset{\displaystyle CH_3}{\overset{|}{CH}}{=}CH{-}CH{=}CH_2$$

Diïsopropenyl or 2·3 dimethyl-butadiene, . . .



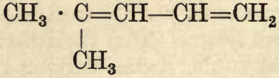
$$CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-\!\!-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH_2$$

Methyl-isoprene (Harries), . .



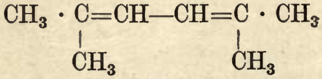
$$CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}CH{=}\underset{\displaystyle CH_3}{\underset{|}{CH}}$$

αα - dimethylbutadiene or trimethylethylene or methyl-2·4-pentadiene, ...



$$CH_3 \cdot \underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH{-}CH{=}CH_2$$

αα-δδ-tetramethylerythrene or 2·5 dimethyl-2·4 hexadiene, . .



$$CH_3 \cdot \underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH{-}CH{=}\underset{\displaystyle CH_3}{\underset{|}{C}} \cdot CH_3$$

Phenylerythrene, . . . $C_6H_5 \cdot CH{=}CH{-}CH{=}CH_2$

The words of Berthelot are thus substantiated; he says that "not only has chemistry the power of rebuilding that which it has destroyed, but it even has the power of forming a host of artificial bodies similar ~~to the~~ natural products, and sharing all their properties, these individual substances being the concrete images of abstract laws made known by analysis."

The synthesis of caoutchouc comprises two distinct problems, which we shall study successively, viz.:—

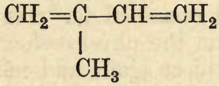
(1) The production of isoprene and analogous hydrocarbons, and the study of their properties.

(2) The polymerisation of these products.

Properties of Isoprene and Allied Hydrocarbons.—We shall first of all give an account of the physical and chemical properties of isoprene and its isomerides, and those of butadiene and dimethyl-butadiene, the only homologues of isoprene which up to now have been utilised for the preparation of synthetic rubbers.

Then we shall study the different methods which have been suggested for the preparation of these compounds.

Isoprene.—Isoprene is a diethenoid hydrocarbon, or di-olefine, the molecule of which contains two conjugated double linkings. It is methyl-2-butadiene 1·3, and has the following constitution:—



$$\begin{array}{l} CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}CH{=}CH_2 \end{array}$$

its elementary composition being C = 88·16; H = 11·84 per cent.

It was first obtained by Himly about 1835, but its characterisation is due to Greville Williams.

It is a mobile liquid, the recorded boiling point of which varies according to the method of preparation—that is to say, according to its degree of purity—from 32° to 37° C.

The following table shows the figures given by various authors for the boiling point and density of isoprene prepared in the different ways indicated:—

AUTHOR.	Method of Preparation.	Boiling Point.	Density.
Greville Williams, . .	Distillation of rubber, .	37 to 38° C.	0·6830 at 20° C.
Berthelot, . . .	Synthesis, . . .	35	0·6823 ,, 0
Bourgouin, . . .	Distillation of rubber, .	45	...
Ipatiew, ...	Synthesis, . . .	32 to 33	0·6742 at 18
Euler, ...	,, . . .	33 ,, 39	...
Tilden, . . . ,	From turpentine, . .	34 ,, 35	0·6742 at 18
,, ...	Distillation of rubber, .	34 ,, 35	0·6766 ,, 18
Blaise and Courtot, . .	Synthesis, . . .	36	...
Harries and Neresheimer,	,, . . .	30 to 37	0·6780 at 19
,, ,,	,, . . .	36 ,, 37	0·6804 ,, 21
,, Gottlob, .	From dipentene, . .	35·5 ,, 36	0·6815 ,, 18·5

It is well known that a definite relationship has been established between the chemical constitution of a compound and its optical properties.

Thus the molecular refraction of a compound can be calculated by taking the sum of its atomic refractions. But atomic refraction is only a constant in the case of monovalent elements; in the case of polyvalent elements it is only the molecular refraction of saturated compounds which is independent of the way in which the atoms are grouped.

In unsaturated compounds the actual molecular refraction is greater than that calculated from the sum of the atomic refractions; in particular the presence of multiple linkages between carbon atoms brings about a constant increase in the molecular refraction; this increase amounts to 2·4 per ethylene linkage, using Gladstone's formula, or 1·84 using that of Lorentz, refraction being measured with reference to the α-line of the hydrogen spectrum.

Without entering into further details, which will be found in the works of Nernst and of Ostwald, we give below the optical constants of isoprene given by Gladstone and Hibbert in their work on caoutchouc and its derivatives:—

Specific refraction, ... $\frac{n-1}{d} = 0{\cdot}592$
Dispersion, ... $= 0{\cdot}0470$
Double bonds, ... $= 2$
Optical formula, ... $= C_5H_8F_2$

Gladstone and Hibbert's remained for a very long time the only work carried out upon rubber from the physico-chemical point of view. Harries took up this aspect of the subject again, and completed their work by a very thorough examination of the optical properties of isoprene.

This substance, being one of the simplest compounds containing conjugated double linkings, considerable interest attached to its study from this point of view. In addition to dispersion and molecular refraction, Harries calculated the values Σ, in accordance with the suggestion of Auwers and Eisenlohr.[1] The latter, by examining the "optical exaltation" produced by certain conjugated linkings, succeeded in establishing a rule according to which—in a general way—the introduction of side chains, or carbon atoms placed in the centre of a secondary conjugated system, diminishes the optical activity. In the case of isoprene the system has only one disturbing factor, the presence of the methyl group as a side chain, and the variation is, therefore, small. But still there were no data as to dispersion. The pure substance, according to Harries, produced an exaltation of 41·3 per cent. for $\Sigma_\gamma - \Sigma_\alpha$, in complete agreement with Auwers' work.

The optical constants obtained by Harries are tabulated below:—

Method of Preparation.	n_D.	MR_D.	$MD_{\gamma-\alpha}$.	Temperature.
Euler's synthesis, ...	1·40777	24·87	1·12	18° C.
Tilden's method from turpentine, .	1·40790	24·84	1·12	18
,, ,, rubber, .	1·40410	24·84	...	18
Harries and Neresheimer, No. 1, .	1·42710	25·02	...	19
,, ,, No. 2, .	1·42267	25·45	1·33	21
Harries and Gottlob from dipentene,	1·42117	25·33	1·25	18/4

By preparing isoprene from the bromide of β-methyltetramethylene and

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[1] *J. f. prakt. Chem.*, 1910, 72, 65; *Ber.*, 1910, 43, 806.

quinoline, a method which will be described presently, Harries obtained a very pure product with the following physical constants :—

Density at 19° C., ... 0·678
Optical constants at 19° C., . . . n_D = 1·41271
,, ,, . . . n_α = 1·40855
,, ,, . . . n_γ = 1·43127
M_D, . . . Calculated, 24·33; found, 25·02
$M_\gamma - M_\alpha$, . . ,, 0·94; ,, 1·20
Σ_D, ... ,, 35·74; ,, 36·82
$E\Sigma_D$ = 1·8.
$\Sigma_{\gamma-\alpha}$, . . . Calculated, 1·39; found, 1·77
$E\Sigma_{\gamma-\alpha}$ = 0·38, or 27·4 per cent.

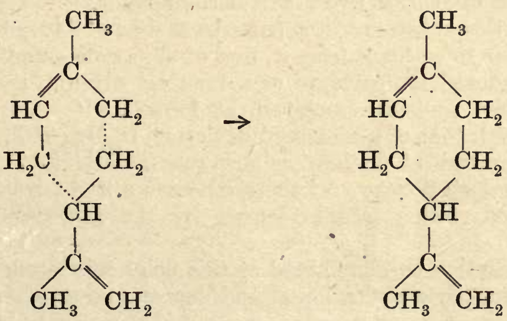
By treating the bromide of β-methyltetramethylene with trimethylamine and distilling the corresponding hydrate, Harries obtained an isoprene having the following constants :—

$D^{21°}_{21°}$ = 0·6804 $D^{21°}_{4°}$ = 0·6793
Optical constants at 21° :—
i_D = 51·10° n_D = 1·42267
i_α = 52·00° n_α = 1·44340
M_D, ... Calculated, 24·33; found, 25·45
$M_\gamma - M_\alpha$, ... ,, 0·94; ,, 1·33
Σ_D, ... ,, 35·74; ,, 37·46
$E\Sigma_D$ = 1·72, or 48 per cent.
$\Sigma_{\gamma-\alpha}$, ... Calculated, 1·386; found, 1·958
$E\Sigma_{\gamma-\alpha}$ = 0·572, or 41·3 per cent.

All the values of Σ are arrived at taking the density as $D^{19°}_{4°} = 0·677$. Isoprene has a very characteristic odour, slightly oniony, sometimes mild and pleasant, according to Harries; this must be dependent on the proportion of an isomeride—dimethylallene—$(CH_3)_2 \cdot C = C = CH_2$, which may be present.

When heated, isoprene is capable of yielding products identical with caoutchouc, and we shall study this conversion later, examining the phenomena of polymerisation; but at the same time it can also give rise to cyclic terpenes, like dipentene and terpilene.

The conversion takes place at temperatures between 270° and 280° C., and is readily explained by Thiele's theory, as the following formulæ indicate :—


2 molecules of isoprene. Dipentene or limonene.

This formula for limonene contains an asymmetric carbon atom, in agreement with the fact that it exists in two optically active forms.

The phenomena of the polymerisation of isoprene to form terpenes are often displayed in the course of the preparation of synthetic rubber from this hemiterpene, and it then becomes necessary to separate these products from the rubber, by distillation under a reduced pressure of 10 mm. of mercury.

These terpene condensation products were first studied by Gustave Bouchardat, who wrote on the subject as follows :—[1]

"I endeavoured to bring about the polymerisation of isoprene without the intervention of substances which might destroy the camphene-like hydrocarbons formed. With this object I heated isoprene in sealed tubes, from which the air had been displaced by carbon dioxide, for ten hours at 280° to 290° C. No gaseous products are formed under these conditions. The product differs entirely, in appearance, from the original isoprene ; it is less fluid, more viscous ; its density has increased, and it no longer boils at a constant temperature of 38° C.

"On distillation it can be split up into three main portions :—(1) A certain amount of unchanged isoprene ; (2) a hydrocarbon volatile at 170° to 180° C. ; (3) condensation products of higher boiling point, including a certain quantity of a hydrocarbon having the composition $C_{15}H_{24}$, and mainly a solid, non-crystalline hydrocarbon, *colophene*, which splits up on distillation at about 300° C. into more volatile hydrocarbons.

"I studied chiefly the product volatile between 170° and 185° C. : the greater part of this passes over between 176° and 181° C. It has an agreeable odour, the onion-like character of the odour of isoprene having disappeared and been replaced by a very strong odour of lemon, approaching that of 'iso-terebenthene,' or turpentine which has been modified by heating. Its density is 0·866 at 0° C., and 0·853 at 21° C. Its composition agrees closely with the formula $C_{10}H_{16}$, 0·218 grm. of the substance giving 0·234 grm. of H_2O and 0·705 grm. of CO_2, which is equivalent to C = 88·2 ; H = 11·9 per cent.

"This compound undergoes rapid alteration when exposed to the air, absorbing oxygen in a manner similar to turpentines ; it is optically inactive.

"Its most characteristic reaction is with hydrochloric acid gas, which combines with the hydrocarbon direct, or, better, when dissolved in ether.

"The residue obtained on evaporating this solvent is, at 20° to 22° C., an oily substance, containing a considerable amount of combined chlorine. This is a mixture of at least two different compounds.

"I distilled this substance in a partial vacuum at 140 mm. of mercury, and was thus able to separate from it, first of all, a compound which remains liquid at the reduced temperature of a freezing mixture, and which boils, under the reduced pressure employed, at 145° C. Its composition agrees pretty closely with that of a monohydrochloride, $C_{10}H_{16}$, HCl.

"The temperature of distillation now rose rapidly to 175° to 180° C., where it remained stationary ; at the same time a slight amount of decomposition occurred, which was evidenced by the liberation of hydrogen chloride.

"If the distillation be interrupted at this point a substance is left in the retort which generally remains liquid and deposits no crystals at the atmo-

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[1] *Bull. Soc. Chim.*, 1875, 24, 112.

spheric temperature of 20° C.; but it is only necessary to keep it by means of a freezing mixture at −10° C. to cause it to solidify completely. Sometimes solidification does not take place at once, and must be started by adding a trace of the substance already isolated, or even of the crystalline hydrochloride of turpentine. The crystals are separated from the mother-liquor by pressing the mass at a low temperature, and are purified by crystallisation from ether, further pressing, and recrystallisation.

"The substance thus purified is found to possess all the properties of terpilene hydrochloride. It melts at 49·5° C., and solidifies again at about 43° C.

"It contains 33·75 per cent. of chlorine, 57·3 per cent. of carbon, and 8·9 per cent. of hydrogen, which figures correspond to the formula $C_{10}H_{16}$, 2HCl; finally the crystals are isomorphous, and probably identical, with those of turpentine dihydrochloride, or terpilene hydrochloride. The identity of the two substances is strongly confirmed by the fact that the addition of a trace of the dihydrochloride, prepared from turpentine, to the oil referred to above brings about the crystallisation of my new dihydrochloride from the superfused mass. The hydrochloride of caoutchine similarly promotes crystallisation.

Lastly, it may be added, with the aid of this dihydrochloride it is quite easy to reconstitute terpilene, $C_{10}H_{16}$, which is isomeric with turpentine, and can be prepared from it by fixing the molecular state of the hydrocarbon by means of its compound with two molecules of hydrogen chloride.

"To sum up, isoprene, a hydrocarbon containing five equivalents of carbon, yields by condensation under the influence of heat a hydrocarbon containing double the amount of carbon, whose derivatives are identical with those of terpilene.

"These facts are sufficient, in my opinion, to show that this terpilene and the camphene hydrocarbons from which it is derived—such as turpentine, lemon essence, the various $C_{10}H_{16}$ hydrocarbons contained in naturally occurring essential oils which have been modified by combination with hydrogen chloride—that all these hydrocarbons are polymerides, $(C_5H_8)_2 = C_{10}H_{16}$, of certain hydrocarbons of the formula C_5H_8, in the same way as benzene is derived from three molecules of acetylene, condensed to form a single molecule."

This formation of dipentene from isoprene is exceedingly interesting. Since the former is the chief product of the dry distillation of rubber, as we shall see presently, it is easy to understand that the caoutchouc must first of all be decomposed into dimethyl-*cyclo*-octadiene, which in turn breaks down into isoprene, the latter condensing again almost at once, under the influence of heat, to form dipentene, in the manner so clearly explained by Bouchardat.

This is, moreover, the view expressed by Harries in his lecture in Vienna, when he said: "It is logical to suppose that by appropriate depolymerisation of caoutchouc, carried sufficiently far, one should be able to arrive at the primitive hydrocarbon—dimethyl-*cyclo*-octadiene—or isoprene. I have made many experiments with this end in view. In particular, prolonged heating of caoutchouc in toluene or xylene brings about depolymerisation; but the true product which should, according to my theory, be formed—dimethyl-*cyclo*-octadiene—was not obtained, probably on account of its instability. In its place allied substances were produced, such as dipentene and other terpene hydrocarbons."

Greville Williams noticed that, when bromine reacts with isoprene, combination often takes place with explosive violence. Tilden obtained by this reaction a compound having the formula $C_5H_8Br_4$, a yellow oil which does not solidify at —18° C.

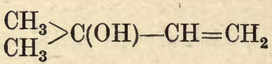
On adding a solution of bromine in carbon disulphide to isoprene at 0° C., two atoms of halogen combine with the hydrocarbon forming $C_5H_8Br_2$, a compound obtained by Bouchardat, and described by Mokiewsky,[1] and by Blaise and Courtot.

This dibromide is a mobile liquid boiling without decomposition at 101° C., at 19 mm. pressure. Its constitution is not yet agreed upon.

The action of the halogen acids was investigated by G. Bouchardat in the course of his work on the polymerisation of isoprene to caoutchouc. Independent of their condensing action, these acids form additive compounds with isoprene.

With dry hydrogen chloride in the cold the following are obtained :—

1. *A monohydrochloride*, C_5H_8, HCl, which boils between 86° and 91° C. Moist silver oxide converts this into a tertiary alcohol, $C_5H_{10}O$, which was investigated by Gadziatsky, who ascribed to it the following constitution :—



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C(OH)—CH=CH_2$$

This alcohol boils at 175° C.

The monohydrochloride reacts with bromine, which combines at the remaining double bond. With excess of hydrogen chloride the monohydrochloride is converted into dihydrochloride.

2. The *dihydrochloride*—$C_5H_8(HCl)_2$—a liquid boiling at 145° to 153° C.

With aqueous hydrochloric acid in the cold isoprene yields the dihydrochloride, together with a monohydrochloride which differs from that already described. This compound is a liquid, with a density of 0·885 at 0° C., and a constant boiling point of 91° C.

It is isomeric with the hydrochloride obtained by the action of gaseous hydrogen chloride, and, like it, is converted into dihydrochloride by the action of excess of hydrogen chloride.

With hydrogen bromide and iodide, formic acid, and acetic acid, corresponding derivatives are obtained.

When heated with aqueous hydriodic acid isoprene is converted, according to Wittorf, into the isomeric dimethylallene :—

$$CH_2=C(CH_3)—CH=CH_2 \rightarrow CH_3—C(CH_3)=C=CH_2.$$

The compounds of isoprene with hydrogen bromide are of similar character to those obtained with hydrogen chloride. They are :—

1. *A monohydrobromide*, C_5H_8, HBr, boiling between 104° and 108° C., and having a density of 1·192 at 0° C.

When treated with moist silver oxide, this compound gives the same tertiary alcohol as the monohydrochloride. It combines additively with two atoms of bromine.

2. *A dihydrobromide*, $C_5H_8(HBr)_2$, boiling at 108° C., and having a density of 1·623 at 0° C. With alcoholic potash this compound loses half its bromine and is converted into a liquid boiling at 110° C. According to Wittorf, it has the same structure as the dibromide of α-dimethyltrimethylene :—

$$CH_3—C(CH_3)Br—CH_2—CH_2Br,$$

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[1] *J. Russ. Soc.*, 1898, 30, 885. *Centralblatt*, 1899, 1, 590.

which can also be obtained by direct combination of hydrogen bromide with unsymmetrical dimethylallene—

$$(CH_3)_2C{=}C{=}CH_2.$$

This is a very important point in connection with the constitution of isoprene, and we shall return to it. Wittorf prepared isoprene hydrobromide by the interaction of bromine, in acetic acid solution, with isoprene obtained by the destructive distillation of pure Para rubber.

This hydrobromide, whether obtained from isoprene or from dimethylallene, has the same physical constants, and, in particular, yields the same dimethyltrimethylene glycol, boiling at 201° C.

Whatever its origin, it also gives exactly the same reactions with alcoholic potash. The reaction starts with explosive violence, but soon slows down and proceeds smoothly, and results in the production of a hydrocarbon, C_5H_8, boiling at 32° C., and showing none of the reactions with salts of copper and silver characteristic of acetylene hydrocarbons; it has also the "oniony" odour of isoprene. It interacts with hydrogen bromide, forming the original hydrobromide.

The action of hydrogen iodide upon isoprene is similar to that of the other halogen acids—that is to say, a *mono-* and a *di*-hydriodide are formed, together with an elastic polymeride similar to caoutchouc.

The mixture of hydriodides is a heavy, oily liquid, which is formed in the cold, and can only be fractionated with difficulty, since very marked reduction occurs at 100° C. With hypochlorous acid isoprene combines to form two chlorhydrins, which have been investigated by Mokiewsky.

The *monochlorhydrin* is of no special interest.

The *dichlorhydrin* is similar to the crystalline dichlorhydrin of an erythritol investigated by Mokiewsky: it melts at 81° C.

According to this author, if isoprene be heated in a sealed tube at 120° C., with one molecular proportion of water and two of bromic acid, a dibromoglycol of isoprene is obtained; this is a crystalline substance, melting at about 59° C., and has the empirical formula $C_5H_8O(Br\,.\,OH)_2$.

Greville Williams found that, after several months' exposure to the action of atmospheric oxygen, isoprene becomes viscous;[1] it absorbs oxygen and thus acquires bleaching properties, decolourising indigotin sulphate, and converting lead sulphide into sulphate. After a long exposure, as both Greville Williams and Tilden found, to the action of oxygen, and probably of ozone, a white substance is formed, which can be isolated by distillation. It is explosive, spongy, and elastic; the temperature rise, due to its formation, is very considerable.

Greville Williams' analytical results were as follows:—$C = 78{\cdot}8$, $H = 10{\cdot}7$, $O = 10{\cdot}5$ per cent. C_5H_8O requires $C = 78{\cdot}97$, $H = 10{\cdot}52$, $O = 10{\cdot}54$ per cent.

This oxidation product, therefore, probably has the formula C_5H_8O.

This process of ozonisation was taken up again by Heinemann with a view to the production of caoutchouc.

With concentrated sulphuric acid isoprene gives a blood-red colouration, which disappears on dilution with water; this reaction is identical

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[1] *Phil. Trans.*, 1860, 150, 245; *Proc. Roy. Soc.*, 1860, 10, 516.

with that employed by Wallach to characterise the terpenes; it is probable that sulphuric acid brings about the polymerisation of isoprene to dipentene.

Isoprene combines with sulphur dioxide, forming a white solid, which decomposes on heating, yielding isoprene again.

With fuming nitric acid, according to Harries' experiments, isoprene gives first of all a red, then a deep brown colouration; after a certain time the liquid becomes hot, a violent reaction sets in, and resinous products are formed. There is probably a partial formation of nitrosites. By the action of nitrogen peroxide on isoprene Wallach obtained a crystalline compound, which up to the present time has been only imperfectly investigated.

With nitrosyl chloride, which Tilden employed with a view to the synthesis of caoutchouc, isoprene forms a crystalline derivative, melting at 81° to 82° C.

With formic acid a formic ester is produced, and this, when decomposed by alcoholic potash, gives a hydrate of isoprene.

With acetic acid an acetate is formed, which, on saponification, is converted into the original hydrocarbon. Cuprous chloride and silver nitrate are without action.

Isoprene hydrate, $C_5H_{10}O$, or *methyl-2-butadiene-*1·3-*ol.*, was obtained by Bouchardat by the action of moist silver oxide or of potash on an isoprene monohydrochloride. It is a liquid with a pleasant odour, sparingly soluble in water, insoluble in amyl alcohol, and boiling between 120° and 130° C. It is isomeric with the ethylvinylcarbinol obtained by Wagner, by the action of zinc ethyl on acrolein, and by Harries from acrylic ether and magnesium ethyl iodide by Grignard's method. Bouchardat regarded it as an unsaturated alcohol, and classed it with the alcohols of the ethylene series, without giving its structural formula. Gadziatsky[1] showed that Bouchardat's alcohol is a tertiary, unsaturated alcohol, having the formula

$$(CH_3)_2C(OH) \cdot CH{=}CH_2,$$

and he named it *isoprenic alcohol*, or *dimethylvinyl carbinol*.

According to Menschutkin, however, it is a secondary alcohol of the formula

$$CH_2{=}C(CH_3) \cdot CH(OH) \cdot CH_3.$$

The researches of Mokiewsky,[2] Ipatieff, and Wittorf[3] showed that Gadziatsky's theory was correct, but these authors found that the isoprenic alcohol was always mixed with tertiary amyl alcohol, and that it had a tendency to decompose when heated.

There has been a great deal of discussion about the constitution of isoprene, and it is not without difficulty that it has been settled.

Greville Williams and Bouchardat had given to it the empirical formula C_5H_8;[4] Tilden was the first to propose—in 1882—the structural formula, $CH_2{=}CH(CH_3){-}CH{=}CH_2$, which makes of it a β-methylbutadiene. Tilden's suggestion was based rather upon theoretical considerations than on experimental data.

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[1] *J. Russ. Soc.*, 1886, 18, 318; 1888, 20, 355.

[2] *J. Russ. Soc.*, 1895, 27, 516.

[3] *J. Russ. Soc.*, 1896, 28, 315.

[4] *Chem. News*, 1882, 46, 109.

A variety of later investigations have demonstrated the accuracy of his hypothesis.

Kondakow, in 1888, showed[1] first of all that, starting with the unsaturated monohydrochloride, which he obtained by chlorinating trimethylethylene or ordinary amylene,

$$(CH_3)_2C{=}CH{-}CH_3,$$

and heating it with alcoholic potash at 150° to 160° C., a hydrocarbon, boiling at 33° to 35° C., was obtained, which could be characterised by means of its halogen hydride derivatives, and which was none other than isoprene. Gadziatsky, according to Wolkoff,[2] conceived the same idea, but did not put it into practice. He gave to isoprene the formula

$$CH_2{=}C(CH_3){-}CH{=}CH_2,$$

which is identical with Tilden's formula.

In order to justify this opinion, he had studied the reaction involved in the preparation of chloroamylene, by means of hydrogen chloride,

$$CH_2{=}C(CH_3){-}CHCl{-}CH_3,$$

and he had found that isoprene, when heated with a dilute solution of hydrogen chloride in alcohol, yields an isomeride, unsymmetrical dimethylallene, in accordance with the following equations :—

$$(1)\ \underset{\text{Isoprene.}}{CH_2{=}C(CH_3){-}CH{=}CH_2}+HCl \rightarrow (CH_3)_2C \cdot Cl{-}CH{=}CH_2.$$

$$(2)\ (CH_3)_2C \cdot Cl{-}CH{=}CH_2 \rightarrow (CH_3)_2C{=}C{=}CH_2+HCl.$$

Unfortunately, Gadziatsky was unable to complete these investigations, and it was Wolkoff who took them up and published them.

The structure of isoprene dihydrochloride was established by Kondakow[3] in 1889. He demonstrated the identity of this dihydrochloride of isoprene (Bouchardat) with the dihydrochloride of dimethylallene, both products being derived from β-dimethyltrimethylene glycol. A similar research was carried through with the hydrobromides, by Ipatiew and Wittorf, as we shall show presently.

Tilden's formula for isoprene, $CH_2{=}C(CH_3) \cdot CH{=}CH_2$, had received a certain amount of experimental support when the structure of Bouchardat's and Gadziatsky's isoprenic alcohol was established as

$$CH_3{-}C(CH_3)\,(OH){-}CH{=}CH_2,$$

but since Kondakow had obtained this alcohol from dimethylallene, and since Gadziatsky had shown that isoprene underwent isomeric change to dimethylallene when treated with alcoholic hydrogen chloride, Tilden's and Gadziatsky's hypotheses lost somewhat of their experimental basis.

By producing synthetic isoprene starting with an unsaturated hydrochloride, $CH_2{=}C(CH_3){-}CHCl{-}CH_3$, the structure of which is clearly established, and under conditions which exclude all possibility of isomeric change, Kondakow obtained further confirmation of Tilden's hypothesis. The

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[1] *J. Russ. Soc.*, 1888, 20, 706.

[2] *J. Russ. Soc.*, 1888, 20, 706.

[3] *J. Russ. Soc.*, 1889, 21, 39.

compound, $CH_2{=}C(CH_3){-}CHCl{-}CH_3$, on losing HCl, can only form a closed trimethylene ring compound or else a hydrocarbon having the constitution $CH_2{=}C(CH_3){-}CH{=}CH_2$. Tilden's formula was again confirmed by the work of Ipatiew and Wittorf.[1]

These authors showed that when caoutchouc was subjected to dry distillation, trimethylethylene, or ordinary amylene, $(CH_3)_2C = CH{-}CH_3$, was formed, in addition to isoprene; this compound Mokiewsky had also obtained, starting with turpentine. By the action of hydrogen bromide, in acetic acid solution at low temperature, on isoprene prepared by pyrogenic decomposition, they obtained a dibromide of α-dimethyltrimethylene (mixed with tertiary amylbromide, which could be easily separated by fractional distillation at 74° C. under a reduced pressure of 10 mm. of mercury)

$$(CH_3)_2C \cdot Br{-}CH_2{-}CH_2Br.$$

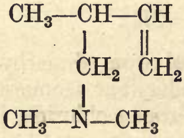
This compound can also be obtained by the addition of hydrogen bromide to unsymmetrical dimethylallene, $(CH_3)_2C{=}C{=}CH_2$.

When treated with hypochlorous acid, dimethylallene gives the same dichlorhydrin, melting at 81° C., as isoprene (Mokiewsky).

Since isoprene and dimethylallene both yield the same derivative with one molecule of hydrogen bromide—viz., $(CH_3)_2CBr{-}CH{=}CH_2$, isoprene can only have the constitution assigned to it by Tilden.

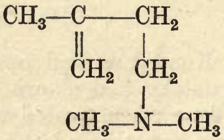
This constitution is confirmed by Euler's synthesis,[2] in which the method employed by Ciamician and Magnaghi[3] for the preparation of erythrene is made use of. Euler converted β-methylpyrrolidine into the methiodide of dimethylpyrrolidine—

On removal of hydrogen iodide from the latter a base was obtained which, by analogy with certain allied derivatives obtained by Ladenburg, should be made up of two isomerides :—



$$\begin{array}{ccc} CH_3{-} & CH{-} & CH \\ & | & \| \\ & CH_2 & CH_2 \\ & | & \\ & CH_3{-}N{-}CH_3 & \end{array}$$

and



$$\begin{array}{ccc} CH_3{-} & C{-} & CH_2 \\ & \| & | \\ & CH_2 & CH_2 \\ & & | \\ & & CH_3{-}N{-}CH_3 \end{array}$$

The methiodide of this base was decomposed by alcoholic potash, yielding trimethylamine and isoprene, identical in its properties with that obtained by the destructive distillation of rubber.

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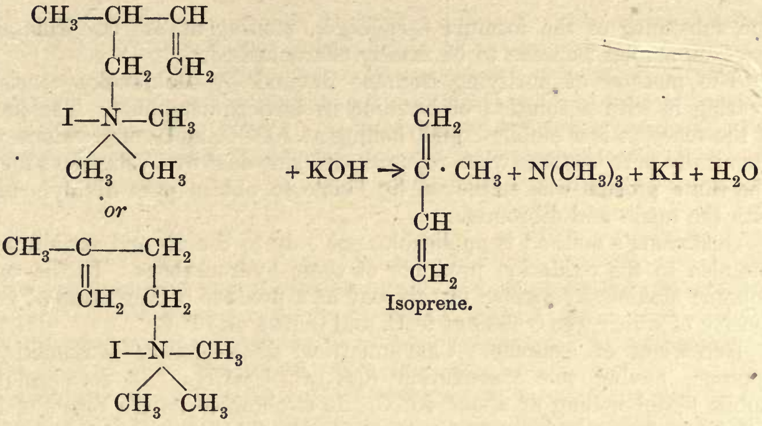
[1] *J. pr. Ch.*, 1897, 55, 4.

[2] *Ber.*, 1897, 30, 1989.

[3] *Gazz. chim. Ital.*, 1895, 15, 485.

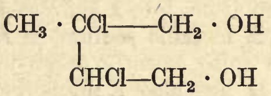


$$\begin{array}{l}CH_3—CH—CH\\ \quad\;\; |\quad\;\; \|\\ \quad\;\; CH_2\;\; CH_2\\ \quad\;\; |\\ I—N—CH_3\\ \quad / \;\; \backslash\\ CH_3\;\; CH_3\\ \quad\;\; or\\ CH_3—C——CH_2\\ \quad\;\; \|\quad\;\; |\\ \quad\;\; CH_2\;\; CH_2\\ \qquad\qquad |\\ \qquad I—N—CH_3\\ \qquad\quad / \;\; \backslash\\ \qquad CH_3\;\; CH_3\end{array} + KOH \rightarrow \begin{array}{l}CH_2\\ \|\\ C\cdot CH_3\\ |\\ CH\\ \|\\ CH_2\end{array} + N(CH_3)_3 + KI + H_2O$$

Isoprene.

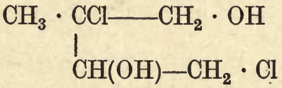
The more recent work of Mokiewsky, again, serves to confirm Tilden's views as to the constitution of isoprene. Mokiewsky succeeded in preparing successively the following derivatives of isoprene :—

(1) A dichlorhydrin



$$\begin{array}{l}CH_3\cdot CCl——CH_2\cdot OH\\ \qquad\;\; |\\ \qquad\;\; CHCl—CH_2\cdot OH\end{array}$$

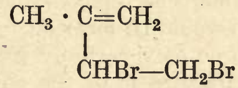
or



$$\begin{array}{l}CH_3\cdot CCl——CH_2\cdot OH\\ \qquad\;\; |\\ \qquad\;\; CH(OH)—CH_2\cdot Cl\end{array}$$

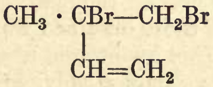
(2) A dibromhydrin of similar constitution.

(3) A dibromide



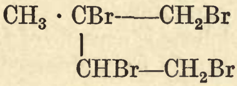
$$\begin{array}{l}CH_3\cdot C{=}CH_2\\ \qquad\;\; |\\ \qquad\;\; CHBr—CH_2Br\end{array}$$

or



$$\begin{array}{l}CH_3\cdot CBr—CH_2Br\\ \qquad\;\; |\\ \qquad\;\; CH{=}CH_2\end{array}$$

(4) A tetrabromide



$$\begin{array}{l}CH_3\cdot CBr——CH_2Br\\ \qquad\;\; |\\ \qquad\;\; CHBr—CH_2Br\end{array}$$

the formation of all of which is well explained by the formulæ given.

To Mokiewsky's investigations quite a special interest attaches, for by examining successively the behaviour of isoprene towards hypochlorous and hypobromous acids, as well as towards bromine, he obtained information of fundamental importance with regard to the nature of isoprene, from which he was able to confirm :—

(1) The accuracy of the structural formula, $CH_2{=}C(CH_3)—CH{=}CH_2$, assigned to isoprene by Tilden.

(2) The presence of trimethylethylene, which was also pointed out by Ipatiew, in the isoprene obtained by the destructive distillation of rubber.

From these investigations Mokiewsky also deduced a method of characterising isoprene by means of hypochlorous acid, as well as a method for purifying this hydrocarbon.

By the addition of two molecules of hypochlorous acid to isoprene, a dichlorhydrin—methyldichlorobutane glycol—is obtained ; this is a crystalline substance of the formula $C_5H_{10}O_2Cl_2$, melting at 81° C. This simple reaction enables isoprene to be readily characterised.[1]

The method of purifying isoprene devised by Mokiewsky consists in treating it with a solution of bromine in carbon disulphide. The product of the reaction is a mobile liquid, boiling at 100° C. at 19 mm., which yields chemically pure isoprene when reduced with zinc dust by Gustavson's method. The same process was employed by Thiele to obtain pure divinyl, starting with the tetra- and dibromide.

Gustavson's method is applicable, not only to the di- and tetrabromides, but also to the oxidation products of these hydrocarbons. In the case of isoprene Mokiewsky arrived in this way at a product boiling at 33·5° C., the density of which was 0·6989 at 0° C. and 0·6794 at 19° C.

Isomerides of Isoprene.—Unsymmetrical *dimethylallene* is isomeric with isoprene, having the constitution $(CH_3)_2C{=}C{=}CH_2$. It is a colourless mobile liquid boiling at about 40° C. It is obtained as the result of intramolecular change in isoprene, as we have already seen, and also by a similar change in an acetylene hydrocarbon, isopropylacetylene, $(CH_3)_2CH{-}C{\equiv}CH$. The carbon atom next the acetylene linkage is attached to only one hydrogen atom, and by the action of alcoholic potash this hydrocarbon is transformed, by migration of a hydrogen atom, into a hydrocarbon of the type of *allene*.

This, when heated with metallic sodium, is reconverted into isopropylacetylene. Lebedeff[2] has quite recently taken up the study of this little-known compound again, as has also Koutcheroff. The latter noticed that when dimethylallene is heated in a sealed tube with quinoline hydrobromide it is isomerised to isoprene.

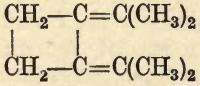
From the standpoint of the synthesis of caoutchouc the fact was of interest, for it contained the germs of a method for preparing isoprene starting with isopropylacetylene.

Lebedeff thought that on polymerising dimethylallene products identical with those obtained from isoprene would be formed.

This hypothesis has proved to be only partially true, for simultaneously there occurs a polymerisation, characteristic of the allenes, the products of which are derivatives of cyclobutane.

Theoretically, dimethylallene is capable of forming six different dimerides, only two of which have actually been obtained, viz. :—

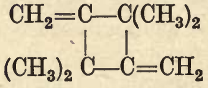
(1)



$$\begin{array}{l} CH_2{-}C{=}C(CH_3)_2 \\ \,|\qquad\ | \\ CH_2{-}C{=}C(CH_3)_2 \end{array}$$

Boiling point, 61° to 62° C. at 9 mm.

(2)



$$\begin{array}{l} \qquad\ \ CH_2{=}C{-}C(CH_3)_2 \\ \qquad\qquad\ \ |\quad\ | \\ (CH_3)_2\,C{-}C{=}CH_2 \end{array}$$

Boiling point, 37° to 38° C. at 9 mm.

A third could not be isolated on account of its high velocity of polymerisation, but its existence was considered certain,[3] and by simply heating the monomeride at 120° C. for three days, Lebedeff has latterly succeeded in obtaining it. It is a colourless liquid with the odour of turpentine, boiling at 140° C.,

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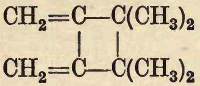
[1] Ipatiew and Wittorf, *J. pr. Chem.*, 1894, 50, 1.

[2] *J. Russ. Soc.*, 1911, 43, 820.

[3] *J. Russ. Soc.*, 1912, 44, 1735.

and having the following physical constants :—$d_{20^\circ} = 0{\cdot}7927$; $n_D^{20^\circ} = 1{\cdot}46063$; $R\,M_D = 45{\cdot}24$ calculated for $2\,F = 57{\cdot}05$.

When allowed to stand at ordinary temperature it deposits an amorphous precipitate; when ozone is passed into a solution in chloroform an ozonide is formed which on hydrolysis yields tetramethylsuccinic acid, pointing to the following constitutional formula for the hydrocarbon :—



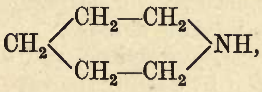
$$\begin{array}{l} CH_2=C-C(CH_3)_2 \\ \quad\;\;\, | \quad\;\; | \\ CH_2=C-C(CH_3)_2 \end{array}$$

The conditions of polymerisation vary according to the temperature employed, and dipentene is produced only if 200° to 225° C. is reached; at lower temperatures only the dimerides mentioned above are obtained.

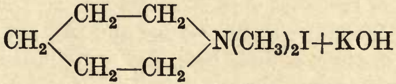
The first of these is a colourless liquid, with an aromatic odour, which oxidises in the air, becoming viscous and yellow in colour; its density at 0° C. is 0·8572; it does not form bromides, but yields an ozonide which is hydrolysed by water to acetone and acetone peroxide.

The second is a colourless liquid, with an odour of kerosene, and a density at 0° C. of 0·8143. It forms an ozonide which on hydrolysis with water yields unsymmetrical dimethylsuccinic acid, formic acid, acetone, acetone peroxide, and an oil composed mainly of two ketones.

Piperylene, $CH_3—CH=CH—CH=CH_2$, is another isomeride of isoprene. It is a diethenoid hydrocarbon, capable, as has been already stated, of polymerising to caoutchouc. It was obtained by Hoffmann on decomposing trimethylpiperidine hydrate by heat, trimethylamine and water being formed at the same time. The reaction is somewhat similar to that by which butadiene is obtained from pyrrolidine, or isoprene from β-methylpyrrolidine. Piperidine



combines with methyl iodide in the cold, forming methylpiperidinium iodide; this salt, when treated with potash, gives methylpiperidine, a tertiary base which combines with methyl iodide to form dimethylpiperidinium iodide. Alcoholic potash reacts with the latter, removing hydriodic acid, but at the same time breaking the chain, and forming dimethylaminopentene according to the equation—



$$\rightarrow CH_2=CH\cdot CH_2\cdot CH_2\cdot CH_2\cdot N(CH_3)_2+KI+H_2O$$

Dimethylaminopentene combines with methyl iodide, forming a quaternary iodide which, when treated with moist silver oxide, is converted into trimethylpiperidinium hydrate—

$$CH_2=CH\cdot CH_2\cdot CH_2\cdot CH_2\cdot N(CH_3)_3\cdot OH.$$

This is converted by heat into piperylene, according to the equation—

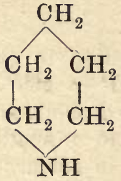
$$CH_2=CH\cdot CH_2\cdot CH_2\cdot CH_2\cdot N(CH_3)_3\cdot OH$$
$$\rightarrow CH_3\cdot CH=CH\cdot CH=CH_2+N(CH_3)_3+H_2O.$$

Piperylene is a colourless liquid boiling at 42° C.

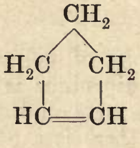
It has no action upon cuprous and silver salts, but interacts with bromine, forming both additive and substitution products, the chief of which is piperylene tetrabromide, which melts at 114° C. without decomposition.

The constitution of piperylene has been much discussed, and the formula given above is due to Laensberg.

Koenigs proposed to substitute for this a ring formula, which would represent piperylene as a 5-carbon ring compound, piperidine having a 6-atom ring nucleus :—



Piperidine.



Piperylene.

Koenigs' formula readily explains the formation of piperylene from dimethylaminopentene, but it does not afford an explanation of the reaction with bromine—the formation of a tetrabromide indicating the presence of two ethylene linkages, whereas the cyclic formula only contains one.

Butadiene.—This compound has hitherto received much less attention at the hands of investigators than isoprene. At first, its importance from the industrial point of view was not recognised, and then it could only be obtained in very small quantity by complicated methods starting from erythritol or butanetetrol, or from pyrrolidine. We shall consider, presently, these different methods of preparation.

Butadiene has the formula C_4H_6, or, structurally, $CH_2{=}CH{-}CH{=}CH_2$, and contains two conjugated double linkings.

It is also called erythrene, pyrrolylene, and divinyl. It was discovered by Caventou, who prepared it by passing the vapour of amyl alcohol through a tube heated to redness.

It is a very volatile liquid; its boiling point is $-5°$ C. when highly purified. It has a characteristic odour, and burns with a smoky flame.

It combines readily with four atoms of bromine, forming two stereoisomeric tetrabromides melting at 118° C. and 39° to 40° C. respectively. Thiele has examined these bromides, and prepares them in the following way :—Crude butadiene is dissolved in twice its volume of chloroform, cooled to a low temperature by means of a freezing mixture of ice and salt; a cold solution of bromine in chloroform is then added, drop by drop, until the colour of bromine persists.

If the temperature is very low, dibromide is formed instead of the tetrabromides. This is a crystalline substance, having the formula

$$CH_2Br{-}CH{=}CH{-}CH_2Br$$

and melting at 53° C.

This is the compound which Griner used in his synthesis of erythritol.

The tetrabromide which melts at 118° C. is re-converted by the action of zinc dust, in presence of boiling alcohol, into butadiene, a reaction which may be employed to obtain the hydrocarbon in a state of purity. If the temperature is not kept sufficiently low during bromination there is formed a liquid dibromide, heavier than water, almost colourless, and distilling between 148° and 158° C. In presence of excess of bromine this compound takes up a further two atoms of the halogen, forming a white crystalline tetrabromide.

This method of bromination has also been applied by Caventou in order to extract from compressed illuminating gas the butadiene which is present in fairly large quantity.

This investigation was taken up again by Colson,[1] who also obtained the tetrabromide of butadiene, by the action of phosphorus pentabromide on erythritol.

Grimaux and Cloez showed that the tetrabromide obtained from the oils of compressed gas and that prepared from erythritol were identical. The tetrabromide is almost insoluble in 85 per cent. alcohol in the cold. It distils between 260° and 270° C., undergoing only slight decomposition. The action of heat is to effect an intramolecular transposition in a portion of the bromine derivative, so that when the distilled product is extracted with petroleum ether a compound melting at 37·5° C. is obtained.

It is regarded either as a tetrabromide of dimethylacetylene,

$$CH_3—CBr_2—CBr_2—CH_3,$$

or as a physical isomeride of erythrene bromide. It crystallises from a saturated solution, in fine, large, monosymmetric plates, which often attain a length of 1 cm.

Ciamician and Magnaghi hold that these tetrabromides are only physical isomerides, and, in their later papers, Grimaux and Cloez show themselves to be adherents to this view.

The last tetrabromide yields, by the action of silver nitrate in acid solution, a compound having the formula

$$C_4H_3 \cdot (NO_2)Br_2(NO_3)_2.$$

Griner's work demonstrated the accuracy of Ciamician's views on the isomerism of the tetrabromides, since by the direct action of bromine on pure erythrene he was able to obtain, simultaneously, the two tetrabromides.

When these were treated with alcoholic potash an oil was obtained which was insoluble in water, soluble in ether and alcohol, and readily volatile in the vapour of the latter.

The oil is only stable in presence of these solvents; the moment it is isolated it becomes converted into a white, amorphous, infusible, insoluble mass, having the composition $n(C_4H_4Br_2)$, and evidently a polymeride of dibromoerythrene.

Bromine is rapidly absorbed by a solution in ether of the unpolymerised compound; the products of the reaction are *dibromoerythrene dibromide*, $C_4H_4Br_4$, a substance crystallising in prisms melting at 67° C., very soluble in alcohol, ether, and light petroleum, and *dibromoerythrene tetrabromide*, $C_4H_4Br_6$, very sparingly soluble in ether and, according to Grimaux and Cloez, melting at about 170° C. with partial decomposition.

On brominating at a low temperature the oils obtained from compressed gas, Griner obtained two stereoisomeric dibromides; one of these is a solid melting at 53° to 54° C., and the other a liquid boiling at 70° C. at 20 mm.

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[1] *Bull. Soc. Chim.*, 1887, 48, 52.

The latter is transformed slowly in the cold, rapidly at 100° C., into a mixture of a solid substance melting at 53° to 54° C., and boiling at 92° to 93° C. at 15 mm., and a liquid with a penetrating odour, distilling at about 70° C. at 20 mm.

On oxidation with permanganate the liquid bromide yields a dibromhydrin melting at 135° C., and the solid dibromide another dibromhydrin melting at 83° C.; the former gives with alcoholic potash Przibytek's butadiene dioxide melting at −15° C., which on hydration yields erythritol.

By heating "*erythritol tetrabromhydrin*" (tetrabromobutane) with bromine in a sealed tube at 175° to 180° C., Colson[1] obtained two hexabromides; the one, a liquid—

$$CBr_3—CHBr—CHBr—CH_2Br$$

is soluble in ether and chloroform, sparingly soluble in alcohol, has a density of 2·9, and when heated with potash in a sealed tube at 120° to 130° C. yields erythric acid together with resinous products; the other, a solid, consists of pearly scales, melting at 169° C., soluble in chloroform, and sparingly soluble in alcohol and ether, and has a density of 3·4.

This product is similar to that obtained by Grimaux and Cloez by exhaustively brominating erythrene dibromide.

Butadiene prepared from erythritol by Henninger's method combines very energetically with chlorine; the reaction can be moderated by allowing the action between the two gases to take place in carbon tetrachloride, and on evaporating the solvent a tetrachloride, $C_4H_6Cl_4$, is obtained, which crystallises in magnificent, very brilliant, colourless crystals, melting at 73° C. and having a characteristic odour.

This compound is identical in its properties, as well as in crystalline form, with the derivative obtained from erythritol.

Starting with Caventou, confusion existed for a long time between butadiene or erythrene and crotonylene, $CH_3—C{\equiv}C—CH_3$, which is prepared from butylene dibromide. These two compounds, although isomeric, are very different substances, and crotonylene is devoid of interest from our present point of view.

There is yet another isomeride of erythrene—viz., butadiene 1·2 or methylallene, $CH_3 \cdot CH{=}C{=}CH_2$—a compound to which little attention has been devoted. Kondakow, as we shall see later, in analysing the work done on polymerisation and the synthesis of caoutchouc, appears to regard as one of the characteristic properties of butadiene and the hydrocarbons of that series, their susceptibility to polymerisation to form bodies either identical with or allied to caoutchouc. This property is the result of the presence in the molecule of two conjugated double linkings, $C{=}C—C{=}C$, which confer upon the compound in question those electronegative properties which render condensation possible.

Dimethylbutadiene.—This substance, which is also called di-isopropenyl or methylisoprene, has the formula $CH_2{=}C(CH_3)—C(CH_3){=}CH_2$. It has been investigated by Couturier,[2] Kondakow,[3] and Mariuza,[4] who obtained

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[1] *Bull. Soc. Chim.*, 1887, 48, 53. Similar treatment of the solid bromhydrin in anhydrous ethereal solution leads to the formation of an isomeric erythritol, crystallising in silky tufts, melting at 72° C.

[2] *Annalen*, 1899, 308, 339.

[3] *Bull. Soc. Chim.*, 1880, 33, 454; *J. f. pr. Chem.*, 1900, 62, 166.

[4] *J. Russ. Soc.*, 1889, 21, 435.

it from pinacone by various methods to be described presently. It is a liquid boiling at 71° C.

Kondakow found the following constants for it :—

$$n_{\mathrm{D}} = 1{\cdot}43751\ ;\ d^{20°}_{20°} = 0{\cdot}7272.$$

Molecular refraction—Calculated, 28·93 ; found, 29·65.

Courtot[1] obtained the following figures :—

$$\text{Density} = 0{\cdot}73074\ ;\ n_{\alpha} = 1{\cdot}4379\ ;\ n_{\delta} = 1{\cdot}4421\ ;\ n_{\beta} = 1{\cdot}4527\ ;$$
$$n_{\gamma} = 1{\cdot}4622\ ;\ \mathrm{M}_{\alpha} = 29{\cdot}45\ ;\ \mathrm{M}_{\delta} = 29{\cdot}70.$$

All these determinations were made at 15° C.

Harries re-determined these constants and found—

$$n^{16\cdot5°}_{\mathrm{D}} = 1{\cdot}44321\ ;\ d^{16\cdot5°}_{4°} = 0{\cdot}7304\ ;\ n^{16\cdot5°}_{\alpha} = 1{\cdot}43870\ ;\ n^{16\cdot5°}_{\gamma} = 1{\cdot}46303.$$

Molecular refraction— M_{D}=Calculated, 28·93 ; found, 29·80.
M_{α}—M_{γ}= ,, 1·054 ; ,, 1·41.

There are several isomerides of di-isopropenyl, viz. :—

Methyl-2-*pentadiene*-1·3, $CH_2{=}C(CH_3){-}CH{=}CH{-}CH_3$.

Methyl-2-*pentadiene*-1·4, $CH_2{=}C(CH_3){-}CH_2{-}CH{=}CH_2$, prepared by Lioubarsky.

(This hydrocarbon does not contain conjugated double linkings, and Weber looked upon it as differing widely from dimethylbutadiene, and as being incapable of polymerisation.)

Methyl-2-*pentadiene*-2·4 or *αα-dimethylbutadiene*,

$$CH_3{-}C(CH_3){=}CH{-}CH{=}CH_2.$$

Hexadiene-2·4, $CH_3{-}CH{=}CH{-}CH{=}CH{-}CH_3$.

Amongst other derivatives of butadiene, the following may be mentioned :—

Dimethyl-2·5-*hexadiene*-2·4 or *αα-δδ-tetramethylerythrene*,

$$C(CH_3)_2{=}CH{-}CH{=}C(CH_3)_2.$$

Dimethyl-2·4-*pentadiene*-1·3, boiling point 90° C.,

$$CH_2{=}C(CH_3){-}CH{=}C(CH_3)_2.$$

Phenylerythrene, $C_6H_5{-}CH{=}CH{-}CH{=}CH_2$, obtained by Klages by decomposing benzylidine-acetone with sulphuric acid ; it is a liquid, boiling at 124° C. at 32 mm. pressure.

Phenylisoprene, $CH_2{=}C(C_6H_5){-}C(CH_3){=}CH_2$, obtained by Courtot, by decomposing dimethylphenyldibromobutyric acid with alkaline carbonates. It is a mobile liquid, with a powerful odour, boiling at 95° C. at 24 mm., and yielding when brominated a tribromo derivative, $C_{11}H_{12}Br_3$, melting at 76° C.

The polymerisation of these latter bodies has only just been attempted ; the caoutchoucs obtained do not appear to be satisfactory substances.

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[1] Thesis, Nancy, 1905, 135.

CHAPTER XII.

METHODS OF PREPARING ISOPRENE AND ITS HOMOLOGUES.

THE methods by which isoprene and the allied hydrocarbons, butadiene and dimethylbutadiene, can be prepared may be classified under three headings :—

(1) Methods involving the destructive distillation of hydrocarbons more complex than isoprene and of some oxygen derivatives, or processes in which certain organic compounds are condensed by heat into isoprene.

(2) Methods which take as their starting point the halogen or hydroxy-derivatives of hydrocarbons which, by the removal of halogen acids or water, respectively, give rise to unsaturated hydrocarbons.

(3) Methods involving the use of nitrogen bases.

In this classification are included purely laboratory methods, as well as processes for which one may hope to find industrial application.

Some of the methods to be described are very fantastic, and appear to be devoid of any scientific value. If we mention them in our list it is merely for the sake of completeness, and in order to give as comprehensive an account as possible of everything that has been put forward in connection with the synthesis of caoutchouc.

Methods of Group I.—Destructive Distillation.—In studying the action of heat on rubber, we gave an account of the work of Himly and Appolinaire Bouchardat, both of whom had isoprene in their hands without suspecting that it was the parent hydrocarbon of polyprene.

In 1860 the subject was taken up by Greville Williams, who isolated and characterised isoprene in the following way :—The distillation of rubber was carried out in an iron flask at a temperature low enough to avoid decomposition ; the crude distillate, which had a very evil odour, due to volatile bases derived from the proteins present in the rubber, was shaken up with dilute sulphuric acid, washed with water, then with caustic alkali, and finally fractionated.

The portion passing over between 37° and 44° C. was crude isoprene. After numerous rectifications over sodium, Greville Williams obtained ultimately a liquid distilling at 37° to 38° C., to which he gave the name of isoprene. It had, on analysis, the following composition :—C = 88, H = 12·1 per cent. C_5H_8 requires C = 88·2, H = 11·8 per cent.

In 1875, Gustave Bouchardat took up the study of the preparation of isoprene, of which his father had previously caught a glimpse.

He says,[1] " I distilled 5 kilos. of Para rubber very recently collected ; it is essential to use new rubber, because this substance is readily oxidisable, and old rubbers give different products on distillation.

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[1] *Bull. Soc. Chim.*, 1875, 24, 108-109.

"After numerous rectifications I obtained—

250 grms. of isoprene.
2,000 grms. of caoutchine, volatile between 176° and 180° C.
600 grms. of heveene, a hydrocarbon volatile between 255° and 265° C.

"The residuc consisted of several other less volatile compounds, of diminishing fluidity, some distilling below 360° C., others decomposing further when heated, reproducing the whole of the preceding series of hydrocarbons.

"In the course of this distillation only a very small quantity of gas (less than 40 litres) was produced; this was composed of carbonic oxide, a little marsh gas, and about 10 grms. of a gas absorbable by bromine, and consisting of a little ethylene and some isoprene vapour.

"In a word, it may be said that caoutchouc is a certain hydrocarbon, $(C_5H_8)_n$, which decomposes when heated into a particular series of polymerides of a single hydrocarbon, C_5H_8; all the other products—and there is not much of them—observed in this distillation, owe their existence either to the presence of impurities or to the break-down of the oxidation products of caoutchouc."

Wallach also studied the dry distillation of rubber. He confirmed the observations made by Greville Williams and Gustave Bouchardat, remarking that isoprene boils at 33° to 38° C., and he showed that the caoutchine, which is formed at the same time, is a polymerisation product of isoprene—viz., a di-isoprene, analogous with dipentene. Ipatiew and Wittorf have pointed out that, in the dry distillation of rubber, trimethylethylene is formed as well as isoprene, and occurs in the fractions distilling above 40° C., a fact which had already been observed by Himly.

The products obtained by Weber on distilling 3 kilos. of Para rubber, purified and dried *in vacuo*, were the following:—

Isoprene, ...	186 grms.	= 6·2	per cent.
Dipentene, . . .	1,380 ,,	= 46·0	,,
Heveene, ...	510 ,,	= 17·0	,,
Polyterpenes, . . .	806 ,,	= 26·8	,,
Carbonaceous residue, . .	59 ,,	= 1·9	,,
Mineral matter, . . .	16 ,,	= 0·5	,,
Loss (moisture and gas),	43 ,,	= 1·4	,,

The quantity of isoprene in Weber's experiments was greater than in those of Gustave Bouchardat. From these results Weber thought it very probable that isoprene is not a direct decomposition product of caoutchouc, but that the latter breaks down in stages under the influence of heat; that a polyterpene of high molecular weight is first formed, then dipentene and finally isoprene; the slower the distillation and the lower the temperature employed, the less dipentene and isoprene is produced, decomposition being progressive.[1]

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[1] This theory is open to discussion when the results of destructive distillation of turpentine are considered; it is probable that direct decomposition of the caoutchouc into isoprene actually takes place, and that the isoprene is at once polymerised to dipentene.

Quite recently E. Fischer and Harries have again submitted caoutchouc to dry distillation, employing a new process, based on the use of the cathodic vacuum. Their apparatus comprises a Geryk vacuum pump, a distilling flask, and a condenser and receiver connected with a Dewar flask cooled in liquid air. On distilling Para rubber, purified by Harries' method, at a pressure of 0·25 mm. pressure, only a little isoprene and dipentene are obtained, the greater part of the distillate being a mixture passing over between 180° and 300° C. Distillation commences, nevertheless, at about 25° C., yielding trimethylethylene, isoprene, and dihydroisoprene.

In the dipentene fraction obtained in another dry distillation, at ordinary pressure, Harries found that on fractionation at 16 mm. four fractions were obtained, boiling respectively at 50° to 60° C., 60° to 65° C., 65° to 70° C., and 70° to 80° C. On rectification three fractions could be separated, one of which was pure dipentene. One of the others, after drying over metallic sodium, boils at about 147° to 150° C. at ordinary pressure; it is a colourless oil, with a pleasant smell, and has the following physical constants:—

$D_{20\cdot5^\circ}$,	0·8286
$n_D^{20\cdot5^\circ}$,	1·4962
Molecular refraction,	45·24
Calculated $C_{10}H_{16}$ for 2,	44·92
,, ,, 3,	46·94

The last fraction, when dried over sodium, boils at 168° to 169° C.; it is a colourless oil, with an odour of dipentene, and gives a characteristic violet colouration with bromine. It has the following physical constants:—

D_{20°,	0·8309
$n_D^{20^\circ}$,	1·46856
Molecular refraction,	45·54

We have dwelt at some length upon the preparation of isoprene by the destructive distillation of rubber, because it was the first method discovered for its preparation; for the purpose of a synthesis, seeing what small yields are obtained, it would evidently present no interest, since the object aimed at is the reverse reaction; if, however, the yield of isoprene could be improved, and the whole of the pure rubber contained in a rubber residual could be converted into this hydrocarbon, it would perhaps be of interest to apply this method to waste rubber of low value. The study of vegetable physiology, and the comparison of empirical formulæ, lead to the conclusion that a pretty close relationship must exist between the terpenes and caoutchouc. We have seen that, in the dry distillation of rubber, in addition to isoprene, large quantities of dipentene are formed; but Wallach and others have shown that this substance is definitely derived, by isomeric change, from pinene.[1]

It was possible that all the terpenes which were capable of conversion, by isomeric change, into dipentene, under any influence whatever, might decompose into two molecules of isoprene.

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[1] *Chem. News*, 1882, 46, 129.

Reasoning of this kind led Tilden,[1] in 1882, to attempt to decompose turpentine by heat, by passing its vapour through a red-hot iron tube. He thus succeeded in obtaining methylbutadiene.

Illawitz obtained the same results under the same conditions, but always with exceedingly small yields of isoprene.

In a paper before the Chemical Society of London in 1884,[2] Tilden recognised that turpentine, when vaporised and brought into contact with the walls of an iron tube at a dull red heat, yielded—

(1) Pentine or isoprene, in small quantity.
(2) Heptine.
(3) Metaxylene.
(4) Cymene.
(5) Terpilene.
(6) Benzene.
(7) Toluene.

This work was resumed by Norton and Andrews in the course of an investigation on the production of oil-gas, and these chemists determined that the most favourable temperature for obtaining ethenoid compounds from turpentine appeared to be 800° C., whereas with mineral oils the best temperature to employ seems to be 550° C.

In the latter case the yield of ethylene hydrocarbons amounts to 65 per cent. of the original oil taken. The isoprene content is, unfortunately, always very low, and seems not to exceed 2 to 3 per cent. of the total yield of ethylene hydrocarbons. Nevertheless, it is useful to draw attention to these observations, for they appear to indicate that it is possible, by the destructive distillation of petroleum, to obtain, in addition to traces of isoprene, a mixture of hydrocarbons, rich in methane and ethylene, which could very likely be used as raw material for the production of isoprene or its lower or higher homologues.

The destructive distillation of the terpenes results in rather complex reactions.

The changes evidently take place in several stages. In the first stage the pinene, which constitutes the most important part of turpentine, must be converted, by isomeric change, into dipentene, the structure of which is different. This reaction, brought about by heat, requires 17·5 calories per grm.-molecule, according to Berthelot; dipentene can also be obtained by the action of strong acids on turpentine, at ordinary temperature.

In the second stage, the cyclic nucleus of the dipentene formed is opened under the influence of the increasing temperature, yielding, in theory, two molecules of isoprene.

The following formulæ represent the stages in the reaction, the rupture of the nucleus occurring in the position of the dotted lines :—

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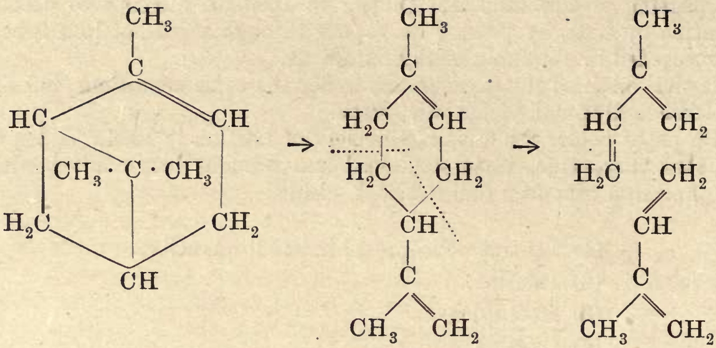
[1] Moreover Bouchardat, by showing that isoprene yields, on polymerisation, di-isoprene, analogous with dipentene, justified this way of thinking, and was the first to establish the connection existing between isoprene and the terpenes. (*Comptes rendus*, 1861, 53, 361.)

[2] *Trans.*, 1884, 45, 490.



Pinene. → Dipentene. → Isoprene.

Hence it will be seen that, in order to obtain a result, the thermal conditions of the reaction must be rigorously observed, for from isoprene, as in the dry distillation of caoutchouc, it is possible to obtain trimethylethylene by reduction—

$$CH_2{=}C(CH_3){-}CH{=}CH_2 \rightarrow CH_3{-}C(CH)_3{=}CH{-}CH_3,$$

and with too high a temperature hydrogen gas never fails to be produced.

As occurred when Schultz desired to repeat Tilden's experiment, other substances may be formed if too much heat be applied, such as for instance colophene, phenanthrene, anthracene, and methylanthracene—compounds the formation of which is evidence of a profound disturbance of the original molecule, and demonstrates the establishment of new equilibria.

The influence of heat is, therefore, many-sided; after having converted pinene into dipentene by isomeric change, and broken the cyclic nucleus of this terpene into two aliphatic chains of isoprene, if it be continued and increased, it is able to bring about the disruption of the substance into its constituent atoms, and to build these up again—either by combination amongst themselves, or by addition to certain portions which remain intact—into new compounds, which tend, through polymerisation and modification of molecular structure, towards increasing complexity. Seeing how unstable the terpenes are as a class, it is easy to suppose that to arrest such a series of modifications at the second stage would be difficult, and one can readily understand the reason for the incompleteness of the conversion of pinene into isoprene. The small yields obtained by Tilden's process are thus explained.

At the time when this method of preparation was worked out, moreover, Tilden was ignorant of the exact temperature at which the decomposition into isoprene could be brought about. He simply stated that it was necessary to proceed "by passing the vapour of pinene through an iron tube heated to redness which is scarcely perceptible in a darkened room."

The work of Ipatiew, carried out in 1897, allowed of a rather more precise determination of the most suitable temperature. The Russian chemist found, in fact, that isoprene polymerises to dipentene at 300° C.; the temperature at which pinene is decomposed into the fundamental hydrocarbon, C_5H_8, should, therefore, be a little lower, say between 270° and 280° C.

Provided this temperature be not exceeded, the following products are obtained on treating turpentine according to Tilden's method :—

(1) Isomeric dipentene, distilling between 170° and 180° C.
(2) Colophene, by polymerisation of turpentine.
(3) Cymene, by dehydrogenation of pinene.
(4) Isoprene.

Mokiewski took up Tilden's experiments, and by passing pinene vapour through a dull red-hot tube, obtained, first of all, a liberation of gas consisting of ethylene and propylene, and then a liquid mass which, when fractionated, gave—

(1) 20° to 30° C.—Butylene.
(2) 30° to 40° C.—Isoprene and trimethylethylene.
(3) 70° to 80° C.—Benzene, and olefine and di-olefine hydrocarbons.
(4) 95° to 110° C.—Toluene and olefines.
(5) 135° to 145° C.—Xylene.

It seems evident that in the pyrogenic decomposition of turpentine there is a critical temperature, which can only be maintained with difficulty, and above and below which a whole crowd of substances other than isoprene are formed.

Harries found a very elegant solution of this problem, of which we shall speak shortly.

Tilden prepared isoprene, not only from turpentine—pinene—under the conditions just described, but also from the isomeric "citrene," which Wallach has since shown to be nothing else than dipentene or limonene.

These three compounds are only active or racemic modifications of the same hydrocarbon ; all of them should, therefore, yield isoprene.

Myrcene, a six-carbon terpene and an aliphatic hydrocarbon, behaves in the same way under the influence of heat ; the long chain breaks up into two smaller ones, an atom of hydrogen changing its position, thus—

$$CH_3{-}C(CH_3){=}CH{-}CH_2 \vdots CH{=}C(CH_3){-}CH{=}CH_2$$

Myrcene.

$$\rightarrow 2[CH_2{=}C(CH_3){-}CH{=}CH_2],$$

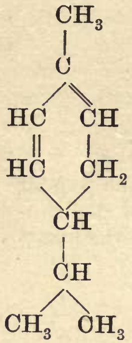
Isoprene.

the rupture occurring at the dotted line.

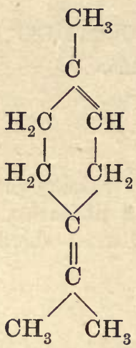
In view of Harries' observations on myrcene and the resemblance of its nitrosite to that of dimethyl-*cyclo*-octadiene, it would not be surprising that this terpene should be an excellent source of isoprene ; unfortunately its price restricts its use to the laboratory, unless it can be produced, by isomeric change, from another terpene.

Sylvestrene will also yield isoprene when decomposed by heat. But most of the quadrivalent terpenes—terpinolene, thujene, terpinene, carvestrene—as well as the divalent terpenes—camphene and bornylene—cannot be dissociated by heat into methyl butadiene, without isomeric change, which occurs with difficulty in certain instances.

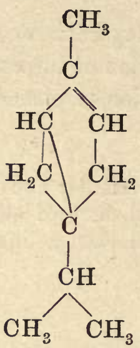
The difficulties are brought out by an examination of their structural formulæ—



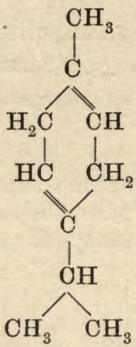
Phellandrene.



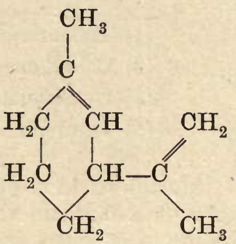
Terpinolene.



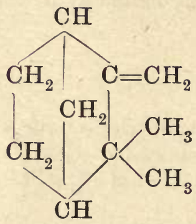
Thujene.



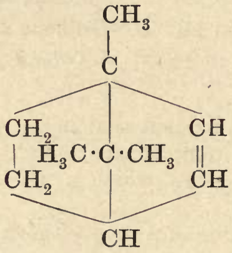
Terpinene.



Sylvestrene
or
Carvestrene.

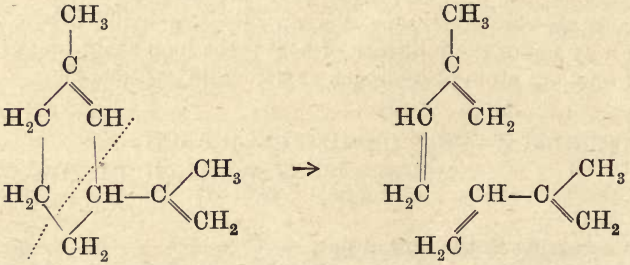


Camphene.



Bornylene.

The formation of isoprene from sylvestrene is easy to understand from the following formulæ, in which the position at which rupture of the ring occurs is indicated by a dotted line :—



Sylvestrene. 2 molecules of isoprene.

The possibility of obtaining isoprene from dipentene and sylvestrene has a certain amount of interest from the technical point of view. Ordinary turpentine, which has already numerous uses in the manufacture of paints and varnishes, is much too costly a raw material, whereas the Russian and Swedish oils obtained by the dry distillation of the stems of conifers, and which are in reality by-products of the manufacture of wood charcoal, afford, by reason of their content of sylvestrene and dipentene, a more advantageous source.

According to Kondakow, Swedish turpentine is especially rich in dipentene, whilst Russian turpentine contains mainly sylvestrene.

The residue, after the removal of bornyl acetate, from the oil of the white Siberian pine (pikita oil) is rich in dipentene, which can be utilised. The same is true of camphor oil, after the safrol has been removed. The white oil is entirely composed of pinene, dipentene, and phellandrene; the red oil contains, in addition, carvacrol, eugenol, and caprylic acid. The liquid products obtained in the preparation of pinene hydrochoride—the raw material of synthetic camphor—by the action of dry hydrogen chloride in the cold, are made up of dipentene hydrochloride mixed with other products. Dipentene can readily be separated from them by suitable treatment with lead salts, for example; here is, therefore, another source either of isoprene or of raw materials capable of yielding caoutchouc by appropriate treatment.

Tilden also succeeded in obtaining a certain quantity of isoprene by passing the vapour of linseed, colza, and, more particularly, castor oil through a red-hot tube, but the purity of the product and also its quantity were much lower than in the case of isoprene obtained from the terpenes.

Nevertheless, in view of the small yield of isoprene from these various substances, Tilden's process would be of little interest, even in the laboratory, without the modifications which have been introduced, more recently, by various workers.

We have shown the importance of temperature, in that up to a certain point the influence of heat is to decompose, and beyond that to bring about new condensations. Constancy of heating conditions for the decomposing tube is, therefore, of the highest importance, and as the temperature demanded is fairly high, it is difficult of achievement whether under laboratory or factory conditions.

Harries and Gottlob[1] have got over this difficulty adroitly by employing a rheostat as the source of heat. In doing this they applied a method akin to that often used, by Sabatier and Senderens, in hydrogenating various compounds, in presence of finely divided nickel, and one which had already been suggested by Bucherer, Haeussermann, and Niethammer,[2] as well as by Kienlen.[3]

Harries and Gottlob's apparatus has been patented under the name of the "Isoprene Lamp." It consists of a spiral of platinum wire, 120 cm. long, and with a resistance of 90 ohms at a moderate red heat, which requires a current of 5 ampères at 220 volts—that is, 1,100 watts. This spiral is placed, somewhat in the manner of the filament of a tantalum lamp, in a glass flask, which serves as a boiling flask for the turpentine or any other terpene. The vapour passes as produced over the platinum spiral at a red heat, and is there decomposed, at any rate partially. The undecomposed portions of the terpene condense in an upright condenser, kept at a temperature above 50° C., their boiling point being between 153° and 170° C., and they fall back into the boiling flask. The isoprene, boiling between 33° and 38° C., remains in the form of vapour, and passes on, to be condensed in a second condenser, cooled by a brine circulation, or else in a Dewar flask.

The crude isoprene collected in this way is then fractionated with the

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[1] *Annalen*, 1911, 383, 228.

[2] *Chem. Zeit.*, 1903, 27, 1597.

[3] *Fabrication electrolytique de la Soude*, 1898, 140.

aid of a Lebel-Henninger column, and the fraction boiling at 36° C. is separated.

This arrangement is very ingenious, since it permits of continuous working, freeing the isoprene from the vapours of non-converted oil, and causing the latter to flow back continuously into the boiling flask. The yield of C_5H_8 is thus greatly improved, and may reach as much as 40 per cent. of the terpene taken.

As might have been anticipated, dipentene gives much better results than pinene. The isoprene thus obtained is almost as pure as the synthetic product, as obtained by Neresheimer's process or by that of the Elberfeld Colour Works.

Prior to Harries and Gottlob, Heinemann, in his work on the preparation of isoprene from terpenes, had recognised that it was necessary to make the hot contact surface as extensive as possible, so as to prolong the action of heat on the terpene vapour. To this end he very judiciously employed metals of high conductivity, such as copper and silver, in the form of powders, which were placed in the heated tube somewhat in the manner of contact masses. Heinemann worked with turpentine vapour, heated to 500° C.[1] It is equally possible that the silver and copper act, not only as conductors of heat, but also as catalysts.

Still earlier, Oswald Silberrad had pointed out the importance of the heating surface in apparatus for the production of isoprene, the decomposition of the terpene occurring with comparatively great sluggishness. The apparatus proposed by him was made up of a series of metal tubes arranged S-fashion, and heated to between 450° and 750° C., the highest temperature being maintained at the point where the vapour entered the series. The turpentine was introduced drop by drop into an iron retort, heated to dull redness, and connected with the decomposition tubes. The latter were connected in turn with a condenser kept below 0° C. by the circulation of cold brine; finally the pressure was maintained by means of a vacuum pump below 70 mm. of mercury.

Staudinger and Klever [2] were in favour of working with a diluted vapour. They tried mixing it with inert gases such as nitrogen, in conformity with the theory of G. Bouchardat, using Harries and Gottlob's platinum spiral as decomposing calorific surface; then they tried reduced pressure, and finally for pinene they substituted various other terpenes. Working at a pressure of 20 to 30 mm., they found that a large proportion of the dipentene taken was converted into isoprene, and on lowering the pressure to 2 or 3 mm. the yield rose to 60 per cent. It is probable that, in a still higher vacuum, obtained by means of a Geryk pump, still better results would be obtained.

The isoprene obtained under these conditions of very low pressure is almost chemically pure, and differing from that previously obtained, contains only very small quantities of trimethylethylene. These experiments show that the vapours of terpinene, terpinolene, and camphene do not give appreciable quantities of isoprene, a result which is in agreement with the theoretical considerations already set forth; consequently the terpenes which are most suitable for the preparation of C_5H_8 are, as has been stated, the various dipentenes. The purer the raw material the better is the yield of isoprene.

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[1] Eng. Pat. 14,040, June 10, 1910.

[2] *Ber.*, 1911, 44, 2212.

The Badische Company has patented a process very similar to that of Staudinger and Klever.[1]

Other inventors use solvents to collect the isoprene; Wallace, for instance,[2] proposes to use acetic acid.

We have already explained the reasons why, quite apart from all improvements in yield, the terpenes are too costly as raw material; search has therefore been made in another direction.

We are not aware that Tilden's experiments on linseed, colza, and castor oil have been carried any further under the improved conditions as to apparatus and method which we have just described; such an investigation would, however, be of great interest. We shall have occasion to revert to this subject in connection with the preparation of butadiene.

When the synthesis of caoutchouc appeared to be leaving the laboratory stage to enter the industrial field—that is to say, about four or five years ago—it was recognised that it would be necessary to have recourse to less costly raw materials than turpentine or terpenes. Resins and resin oils, on account of their relationship with these hydrocarbons, appeared to be likely substances, and Matthews and Strange endeavoured to obtain isoprene from them.[3] By subjecting either colophony, or, better still, resin oil to a very high temperature, these chemists obtained a series of hydrocarbons, from which they isolated isoprene by fractionation.

The old, but very complete work done by Renard[4] on these materials—work in which one of us collaborated—may afford valuable information on the possibility of utilising resins for the preparation, if not of isoprene, then of materials for its preparation. When colophony—the residue obtained in the preparation of turpentine from conifer resins—is heated at 300° to 360° C., it is converted almost completely into oils, leaving a very small residue of light carbon, amounting to not more than 10 per cent. of the original colophony. These oils consist of a mixture of three hydrocarbons, diterebenthyl, $C_{20}H_{30}$; diterebenthylene, $C_{20}H_{28}$; and didecene, $C_{20}H_{36}$.

Diterebenthyl, which appears to be the most interesting of these hydrocarbons from our present point of view, may be regarded as formed by the union of two $C_{10}H_{16}$ molecules, with the loss of two atoms of hydrogen; it seems, then, to be a dipentene, and its conversion into isoprene when heated is readily explained.

It is possible that the reaction would be improved if it were carried out in presence of hydrogen, applying Sabatier and Senderens' reaction. Under these conditions there would be a tendency to re-form dipentene, and the process would then become a Tilden reaction.

Renard investigated the decomposition by heat of this substance, and made the following statement on the subject:—

"When diterebenthyl is introduced, a drop at a time, into an iron tube heated to a degree of redness which is only visible in the dark, only an inappreciable quantity of carbon is formed inside the tube, the proportion of liquid condensed amounts to about 80 per cent. of the diterebenthyl used, and a certain amount of gas, composed of hydrogen, ethylene, and propylene, is given off."

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[1] Fr. Pat. 425,885, of 1911; Eng. Pat. 1,704, of 1911.

[2] Eng. Pat. 19,701, of 1909.

[3] Eng. Pat., 4,620, May 24, 1911.

[4] *Comptes rendus*, 1888; *Moniteur Scientifique*, 1888, 2, 74.

Acetylene is also formed, and it will be understood that, in consequence, these different hydrocarbons can combine one with the other, forming, in a new phase of the reaction, isoprene, by the modification of the molecular structure of the compounds formed.

Of the liquid product, a small portion boils below 70° C., and in it amylene, hexylene, amyl and hexyl hydrides have been found, but only a little pentene, C_5H_8.

Renard concluded, " Diterebenthyl yields, under the influence of heat, a series of products identical with those which make up the essential oils of resins, or with those obtained by Tilden, in the destructive distillation of turpentine."

This statement shows that, prior to Matthews and Strange, Renard had foreseen the possibility of preparing isoprene from colophony and resin oils, and his investigation constitutes a serious anticipation.

From purified resin oil a whole series of compounds can be obtained by fractionation ; the following is a list of them with their boiling-points :—

BOILING-POINTS OF HYDROCARBONS.

HYDROCARBONS.	BOILING-POINTS.
Amyl hydride, C_5H_{12},	35° to 38° C.
Amylene, C_5H_{10}.	35° ,, 40°
Hexyl hydride, C_6H_{14},	64° ,, 66°
Hexylene, C_6H_{12},	67° ,, 70°
Hexahydrotoluene, C_7H_{14},	95° ,, 98°
Heptene, or tetrahydrotoluene, C_7H_{12},	103° ,, 105°
Toluene, C_7H_8,	111°
Hexahydroxylene, C_8H_{16},	120° ,, 123°
Octene, or tetrahydroxylene, C_8H_{14},	129° ,, 132°
Xylene, C_8H_{10},	136°
Hexahydrocumene, C_9H_{18},	147° ,, 150°
Nonene, or tetrahydrocumene, C_9H_{16}.	155°
Cumene, C_9H_{12},	151°
Terebenthene, α, $C_{10}H_{16}$,	154° ,, 157°
,, β, $C_{10}H_{16}$,	171° ,, 173°
Hexahydrocymene, $C_{10}H_{20}$,	172° ,, 173°
Cymene, or methylpropylbenzene, $C_{10}H_{14}$,	175° ,, 178°
m-Ethylpropylbenzene, $C_{11}H_{16}$,	193° ,, 195°
Dioctene, $C_{16}H_{28}$,	260°

BOILING-POINTS OF ALDEHYDES.

ALDEHYDES.	BOILING-POINTS.
Isobutyric aldehyde,	60° to 62° C.
Valeric aldehyde,	96° ,, 98°

BOILING-POINTS OF ACIDS.

ACIDS.	BOILING-POINTS.
Isobutyric acid,	153° to 155° C.
Valeric acid,	173° ,, 175°

The resin oil is composed mainly of the two terebenthenes, α and β, which represent 75 per cent. of its weight; heptene, nonene, and octene constitute another 20 per cent., and the other compounds are, therefore, present in very small quantity. Seeing how rich it is in terpene hydrocarbons, it is easy to understand that resin oil yields isoprene when destructively distilled, just as does turpentine. It is quite possible that, by adopting the precautions suggested by Staudinger and Klever, good yields of isoprene might be obtained from it.

On seeking in the records of earlier work for information on the products to be obtained by the destructive distillation of the terpenes, or of the resins from which they are derived, or of their residuals, such as colophony, the sylvic acids and their salts, it is found that, according to Bruylants, these bodies are capable of yielding, when so treated, if not isoprene and its homologues, at least certain products which can be utilised in the synthesis of rubber. Bruylants[1] dry-distilled calcium pimarate, obtained by neutralising with lime the crude pimaric acid extracted from landais pine resin; he obtained the following products :—

(1) At about 50°, amylene, C_5H_{10}.

(2) Between 97° and 100° C., diethylketone, $(C_2H_5)_2 \cdot CO$, which can also be obtained by simply boiling common rosin with lime.

(3) Between 155° and 165° C., dipentene in abundance.

These are all substances which by appropriate treatment yield either isoprene or its homologues.

The work of Bischoff and Nastrogel,[2] Mach,[3] and Vesterberg demonstrates the interest which attaches to colophony and common rosin, as raw materials for the preparation of hemiterpenes.

All these investigations, which were carried out with quite another object, ought to be repeated solely from the point of view of the production of butadiene derivatives, carrying out the destructive distillation under greatly reduced pressure, and in the presence of an inert gas, such as nitrogen. It is almost certain that the results would be so much the more interesting because no research has been carried out on these lines up to now, and because the substances being dealt with must, by virtue of their composition, yield the products which are being sought after.

Matthews and Strange have also proposed to use copal oil for the preparation of isoprene, but its relatively high price makes its employment out of the question; moreover, the yield of isoprene to be obtained from it is a very poor one.

In Anquetil's process the same raw material is used, as well as derivatives of Kauri gum.[4]

In the varnish industry the object of fusing the resins is to depolymerise these substances and render them more soluble in various solvents. During the fusing, essential oil, mechanically held by the resin, is liberated, together with hydrocarbons resulting from the deep-seated destruction of the organic molecules, and the establishment of new conditions of equilibrium. It is these condensed products which serve for the preparation of caoutchouc by the above-mentioned process.

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[1] *Academie Belge,* 1876, 41, 539.

[2] *Ber.*, 1890, 23, 1919.

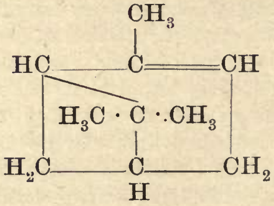
[3] *Monatshefte,* 1893, 14, 186.

[4] Fr. Pat. 441,031.

The useful substances are extracted from the product of condensation by distillation, either dry, or in a current of steam. The object of the operation is the separation of the hydrocarbons with a boiling-point not exceeding 180° C.

After these preliminary operations, the mixture of hydrocarbons contains the following substances :—

(1) A mobile liquid, having a constitutional formula similar to that of true pinene, or α-pinene—



(2) A pentene, C_5H_8, identical with isoprene.
(3) A dipentene, $C_{10}H_{16}$.
(4) Oxidation products.

The pentene is separated by distillation between 25° and 60° C. This product is collected and utilised as explained hereafter. The rest of the liquid is heated and its vapour passed through an iron tube heated to very dull redness—hardly perceptible to the sight—and condensed in the ordinary way.

The fundamental constituents of this new liquid are :—

(1) Isoprene, produced by subdivision into two molecules, of the molecule of the hydrocarbon identical with pinene, mentioned above—

$$C_{10}H_{16} = 2C_5H_8.$$

(2) A terpene isomeric with terebenthene, distilling at about 170° C.

It will be seen that the process is closely allied to that of Matthews and Strange, and the first suggestion of it is contained in Renard's work on the destructive distillation of the resins. We do not think that it has a great industrial future.

Schering [1] proposed *nopinene*, heated at 500° to 520° C. Black and Morton,[2] on similar lines, proposed to employ the resins derived from the treatment of "dead Borneo," or from the purification of resinous rubbers, for the preparation of isoprene. We have seen that these substances are mainly composed of secondary unsaturated alcohols, pretty closely allied to cholesterol; since they contain the vinyl group, it is easy to understand that they may give rise to methyl-divinyls. They may be either destructively distilled, or boiled with caustic alkalies.

According to the Bulletin of the Agricultural Department (1912), isoprene can be obtained by distilling an Australian acaroid resin, obtained from the "grass tree," belonging to the genus Xanthorrhea. This tree is indigenous to the forests of Van Diemen's Land, in Kangaroo Island, as well as in Australia and Tasmania.

This resin is worth from ½d. to ¾d. per lb. in Europe, and is normally imported into Germany for the manufacture of smokeless powders and varnishes.

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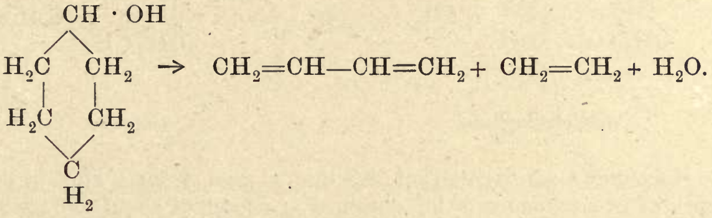
[1] Eng. Pat., Nov. 24, 1909.

[2] Ger. Pat. 241,895, March 12, 1910.

The Bayer Works[1] put forward as a method of preparing isoprene, the destructive distillation of methyl-*cyclo*-hexanol.

This compound, a liquid boiling at about 169° C., is decomposed by passing its vapour through a red-hot iron or porcelain tube, heated at 500° to 600° C., and filled with catalytic material, such as iron turnings or anhydrous alumina[2]; the products formed are, on the one hand, isoprene, and on the other hand, water, and ethylene which can be used, in subsidiary reactions, in order to produce more isoprene or butadiene; the reaction proceeds according to the equation :—

By an analogous method, erythrene can be obtained by introducing *cyclo*-hexanol, drop by drop, into an iron tube heated to 600° C. The reaction is instantaneous and very vigorous :—



$$\rightarrow CH_2{=}CH{-}CH{=}CH_2 + CH_2{=}CH_2 + H_2O.$$

Cyclo-hexanol is easily prepared by the reduction of phenol by the method of Sabatier and Senderens. This method consists in passing phenol over reduced nickel, in presence of excess of hydrogen, at 170° to 200° C. It is a general method, and by the reduction of the homologues of phenol, alkyl-*cyclo*-hexanols are obtained. These alkyl-*cyclo*-hexanols yield substituted butadienes on destructive distillation by the Bayer process.

By this method most of the higher or lower homologues of isoprene can be obtained, starting with a suitably substituted derivative of phenol.

Nevertheless, it must be pointed out that in the reduction process, if the side chains are long, methyl groups are split off, and, according to Sabatier and Senderens, degradation products right down to those containing the methyl group only in the side chain, are produced at the same time as the hexanol, which is the principal product.

On the other hand, since the destructive distillation is carried out at a fairly high temperature, dimerides are formed; for example, in the case

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[1] *J. Russ. Soc.*, 1907, 39, 681. Fr. Pat. 438,789.

[2] Voltereek, Fr. Pat. 423,712, Nov. 28, 1910. The iron tube is filled with substances, the purpose of which is to increase the surface of contact of the vapour with the heated metal; rolls of metallic gauze and perforated discs serve this purpose. The suitable temperature is 550° C. The yield is better with an inert gas like N. The temperature may then be raised to 650° C.

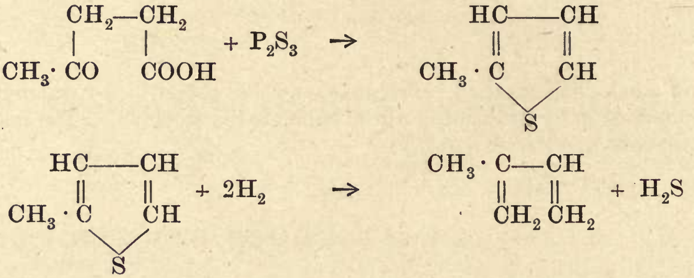
of methyl-*cyclo*-hexanol, since the temperature of the reaction cannot be less than 500° C., and since, according to Ipatiew, isoprene is converted into dipentene at 300° C., unless the passage of the vapour be very rapid the yield of isoprene is exceedingly small.

The reaction can be improved by working with a diluent, under a pressure of 20 mm. of mercury.

Heinemann has put forward a method of preparing isoprene by means of methylthiophene, by passing the vapour of this substance, mixed with excess of hydrogen, over heated copper.

Methylthiophene is prepared by the action of phosphorus trisulphide on levulinic acid. Levulinic acid itself is obtained by Rieschbieth's process —viz., by the action of hydrochloric acid on starch, sugar, or sawdust.[1] The series of reactions is as follows :—

$$(C_6H_{10}O_5)_n \rightarrow CH_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot COOH.$$



Methylthiophene. Isoprene.

Heinemann maintains that, by this process, from 1 kilo. of starch, 112 grms. of caoutchouc can be obtained at a cost of about 2½d., which would appear to be slightly exaggerated.

On the contrary, it is possible, as stated by Ditmar, that no isoprene at all is obtained in this reaction, but rather its isomeride, α-methylbutadiene, otherwise called pentadiene, 1·3. The formation of this compound is, indeed, much more rational, as will be seen on considering the above formulæ. The constitution of methylthiophene is well established; the α-derivative alone can be formed in the reaction between levulinic acid and phosphorus trisulphide. The formation of α-methylbutadiene is very clear :—

α-methylthiophene. α-methylbutadiene.

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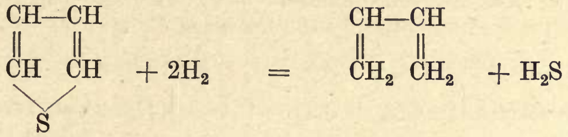
[1] In the preparation of ethyl alcohol by the methods of Simonsen and Claessens—viz., by heating sawdust under 10 atmospheres pressure in presence of dilute sulphuric or sulphurous acid—the cellulose, which is first of all converted into cellobiose, yields, by a secondary reaction on this product, very large quantities of levulinic acid.

β-methylthiophene, on the contrary, would correspond with isoprene :—

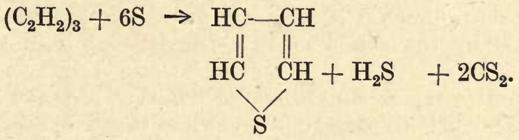
β-methylthiophene. Isoprene.

By subjecting thiophene itself, which can be obtained from coal tar, and from the bye-products of the purification of benzene, to the same treatment, butadiene would be obtained.



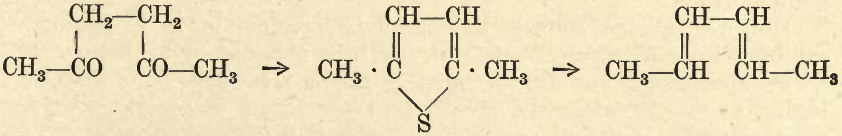
Methylthiophene. Butadiene.

Victor Meyer and Sandmeyer effected the synthesis of thiophene by passing a current of acetylene into molten sulphur.

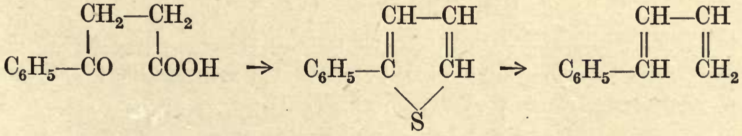


After passing through the sulphur the current of acetylene is led into hot water ; on cooling an oil is deposited which, when washed with alcohol, gives thiophene.

In a similar manner, dimethylthiophene, derived from acetonylacetone, gives rise to hexadiene, 2·4 :—

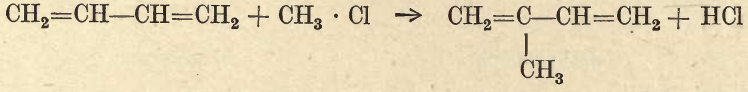


and phenylthiophene, obtained from benzoylpropionic acid, yields phenylerythrene :—



The thiophene compounds, with their two conjugated double linkings, may become of great interest from the point of view of the preparation of isoprene if a practical method for their preparation can be worked out, so as to do away with the delicate use of a sulphide of phosphorus. The process of Victor Meyer, in which the small amount of thiophene which it may contain is extracted from benzene by sulphonation; the improvement, introduced by Schulze, of decomposing the thiophene sulphonic acid by means of water and steam, are more economical; but unfortunately benzene contains only 0·5 per cent. of thiophene. It could not, therefore, become an abundant raw material. Berthelot's experiment,[1] which consists in preparing butadiene by passing a mixture of acetylene and ethylene through a red-hot tube, has long been known. The reaction has been applied by Norton Noyes,[2] and later by Heinemann. The latter obtains divinyl by passing a mixture of the two gases through a red-hot tube. The divinyl is converted into isoprene by the action of methyl chloride, or the latter gas may be passed through the red-hot tube simultaneously with the others. The reaction which occurs is represented by the following equations:—

$$CH \equiv CH + CH_2{=}CH_2 \rightarrow CH_2{=}CH{-}CH{=}CH_2$$



$$CH_2{=}CH{-}CH{=}CH_2 + CH_3 \cdot Cl \rightarrow CH_2{=}\underset{\substack{|\\ CH_3}}{C}{-}CH{=}CH_2 + HCl$$

At the temperature of the reaction it is almost certain that the whole of the isoprene produced is converted into isoprene hydrochloride.

On the other hand, it is difficult to separate the hydrogen chloride, and in order to obtain isoprene it is necessary to prepare first of all the tertiary isoprenic alcohol by the action of silver oxide, and from this to pass to isoprene.

These difficulties raised doubts in the minds of German chemists as to whether it were possible to prepare isoprene and thence synthetic caoutchouc, by Heinemann's method. On this subject Harries remarked, in his lecture at Vienna:—[3]

"I was obliged to repeat these experiments (Heinemann's), and I know that this was done by others; but neither I nor the other chemists have been able to confirm the English patent at all. I do not think the experiment proceeds in this way; our practical trials compel us to regard it as quite unlikely."

However, at the Rubber Exhibition in London, in 1911, Heinemann exhibited isoprene which, he claimed, had been obtained by his process.

De Boistesselin and Dubosc prepare isoprene and erythrene in the following way:—Acetaldehyde, obtained by the action of acetylene on mercuric chloride, is passed over reduced nickel, deposited on asbestos, and heated at 280° to 300° C. It is converted into methane and carbonic oxide, according to the equation—

$$CH_3 \cdot CHO \rightarrow CH_4 + CO.$$

These two compounds can easily be separated by means of cuprous chloride, or the carbonic oxide can be converted into methane by hydrogenation, in presence of reduced nickel, at 200° C.—

$$CO + 3H_2 \rightarrow CH_4 + H_2O.$$

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[1] *Annales de Chimie*, 1867, 9, 466.

[2] *Ibid.*, 1886, 8, 362.

[3] Lecture before the Austrian Association of Engineers, March 12, 1910.

By a classic reaction—viz., by passing the methane over carbon impregnated with copper oxide, at 400° to 450° C., ethylene is obtained, together with propylene and other higher olefines, the proportion of the latter being dependent upon the temperature.

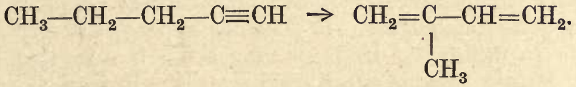
At 400° to 450° C. the proportions obtained are approximately :—

Ethylene,	36 per cent.
Propylene,	42 ,,
Higher olefines and hydrogen,	21 ,,

If to this mixture of gases acetylene be added, the following series of reactions occurs, when the mixture is passed over animal charcoal at 150° C. Propylene combines with acetylene yielding isoprene, in two stages ; in the first stage the two unite to form *normal* propylacetylene,

$$CH_3—CH=CH_2 + CH\equiv CH \rightarrow CH_3—CH_2—CH_2—C\equiv CH,$$

a hemiterpene, which, as observed by Bouchardat, undergoes isomeric change into isoprene on heating—



$$CH_3—CH_2—CH_2—C\equiv CH \rightarrow CH_2=\underset{\displaystyle CH_3}{\underset{|}{C}}—CH=CH_2.$$

Similarly the ethylene combines with acetylene yielding ethylacetylene. The latter, which boils at 18° C., can be separated from the isoprene (boiling point, 38° C.) by fractionation, and can be converted into butadiene by passing it over pumice heated to 300° C.—

$$CH_3—CH_2—C\equiv CH \rightarrow CH_2=CH—CH=CH_2.$$

The originality of this somewhat complex process is centred in the fact that from acetylene only isoprene and butadiene are obtained ; but high yields of these hydrocarbons are prevented by the number of catalytic changes involved. The process belongs rather to the domain of the laboratory than to that of industry.

Since methane is the compound of paramount importance in the series of reactions just explained, any process which permits of the simple production of that hydrocarbon—Sabatier's process, for instance—will be capable of yielding, under the conditions already described, isoprene and butadiene.

It is even possible, in this method of preparation, to make use of ordinary lighting gas, which contains an amount of methane varying from 30 to 40 per cent. ; the methane, nitrogen, carbonic oxide, and carbon dioxide are separated by means of Jouve and Vautier's process of osmotic diffusion. This method, which is applied industrially at the gas works at Lyons, is based upon one of Graham's laws, which states that the velocity of flow of a gas through an orifice pierced in a thin partition is inversely proportional to the square root of its density. The densities of the gases in question are :—

Hydrogen,	0·0896
Carbonic oxide,	1·2510
Methane,	0·5566
Nitrogen,	1·256
Carbon dioxide,	1·966

and it is, therefore, obvious that the hydrogen and methane, which are the interesting constituents from our present point of view, can be readily separated from the other gases which cannot be utilised.

For the purpose of this filtration the material employed may be either glazed porcelain, plaster, graphite, or even sheet metal pierced with holes of a diameter corresponding to the viscosity of the gases to be separated. The apparatus consists of a closed receiver, carrying a series of internal filtering plates. After diffusion through these diaphragms the mixture of hydrogen and methane obtained can be converted into isoprene and butadiene by the method of Du Boistesselin and Dubosc.

Methane can also be prepared from aluminium carbide, Al_4C_3,

$$Al{\equiv}C{-}Al{=}C{=}Al{-}C{\equiv}Al,$$

by Moissan's method. This substance, which is now prepared on an industrial scale, reacts with water to form alumina, which can be worked up again, and methane, according to the equation :—

$$Al_4C_3 + 6H_2O \rightarrow 3CH_4 + 2Al_2O_3.$$

Under these circumstances methane may become an interesting source of isoprene and its homologues. It does not appear that any attempt has been made so to utilise it. Isoprene may again be prepared by isomeric change from certain true or substituted acetylene hydrocarbons, and from allenes.

By the action of alcoholic potash, or of high temperatures, the true acetylene hydrocarbons, such as *normal* propylacetylene, undergo intramolecular change, and are converted into isoprene according to the equation—

$$CH_3{-}CH_2{-}CH_2{-}C{\equiv}CH \rightarrow CH_2{=}C(CH_3){-}CH{=}CH_2.$$

A similar change is undergone by valerylene, pseudo-propylacetylene, δ, and, above all, by dimethylallene. The pyrogenic preparation of butadiene has received little attention. This substance is evidently produced in a manner similar to isoprene, in a considerable number of the reactions to which we have referred, but it ought, more particularly, to be formed in the destructive distillation of the various oils with which Tilden made experiments when investigating the destructive distillation of the terpenes.

In the course of the treatment to which Tilden subjected these oils, decomposition into oil-gas evidently occurred. But this gas is known to contain, in addition to methane, a certain number of hydrocarbons which separate from it when subjected to a pressure of 12 atmospheres. They form the gas-oil from which Faraday separated ethylene, and from which, by bromination, comparatively large quantities of butadiene can be obtained, as shown by Caventou and Cloëz.

An old observation by Théodore Château[1] shows that linseed, colza, and especially castor oil are completely decomposed, and converted almost entirely into hydrocarbons when they are suddenly subjected to a red heat; and he states that unpurified seed oils, crude fish oils, and petroleum residuals may also be employed.

"The retorts or cylinders, in which the decomposition is carried out, are filled with small pieces of coke in order to increase the surface of contact,

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[1] *Corps gras industriels*, p. 14, Edition Hetzel.

and are then heated to dull redness; the oil is then run in in a very fine stream. As soon as it is in contact with the red-hot coke it is decomposed into gaseous products. The reservoir from which the oil is run out serves as a condenser, so that the gas in passing through it deposits any unchanged oil which it may have carried over with it."

It is probable that, by working under reduced pressure, and employing the ingenious apparatus described by Château, it would be possible to bring about a somewhat intensive production if not of isoprene then very likely of butadiene.

As ethylene is certainly formed, and very probably acetylene also, a portion of the butadiene is most likely produced by the condensation of these two gases under the influence of heat, as shown by Berthelot. It is also possible for methylation to occur.

Under these circumstances, oil-gas becomes of great interest as a source of raw materials for synthetic rubber.

The manufacture of the gas is to-day very extensive, and its production —mainly for the lighting of railway trains—is of great importance, since it represents at present the consumption of more than 150,000 coaches.

It will be as well from our present point of view to take a rapid survey of its manufacture.

The oils employed to produce the gas vary a great deal, according to the country in which the manufacture is carried out; vegetable oils, such as castor, earth-nut, and cotton-seed, fish oils, tar oils, shale oil, naphtha, crude petroleum, and petroleum residues rich in naphthenes are all made use of. The apparatus of Seigle and that of Pintsch, which are those most commonly used, consist, in principle, of one or more metal retorts, which are heated to a high temperature, and into which the oil to be decomposed is run in a thin stream.

The average composition of the gas after washing may be taken as—

Paraffins, ...	44 per cent.
Olefines, ...	35 ,,
Carbonic oxide, ...	3 ,,
Carbon dioxide, ...	4 ,,
Hydrogen, ...	11 ,,

According to Groefe, German oil-gas, as made in the Dresden works, has the following composition:—

Vapour of liquid hydrocarbons, . .	1 per cent.
Carbon dioxide, ...	0·4 ,,
Unsaturated hydrocarbons, . . .	24 ,,
Oxygen, ...	0·5 ,,
Carbonic oxide, ...	2·4 ,,
Hydrogen, ...	11 ,,
Methane, ...	40·8 ,,
Ethane, ...	9·9 ,,

This gas is made from lignite tar oil.

The following table is given by Ross and Leather, and shows the composition of the gas obtained by the destructive distillation of various petroleum oils, at about 1,350° C.:—

DISTILLATION OF PETROLEUM OILS (Ross and Leather).

	Solar Oil, Russian.	Solar Oil, Borneo.	Solar Oil, American.	Solar Oil, Texas.	Refined Russian Oil.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Vapour of liquid hydrocarbons,	4·0	4·0	3·2	3·4	3·8
Heavy hydrocarbons, . . .	30·2	22·8	33·0	26·8	28·0
Methane, ...	54·2	60·0	52·5	56·2	57·0
Hydrogen, ...	12·0	13·6	11·6	13·4	11·5

With crude petroleum decomposed at 900° to 1,000° C.—that is, at the melting point of calcium fluoride—Noyes, Blinks, and Mory[1] found that the gases produced had the following composition:—

Carbon dioxide, ...	2·3	per cent.
Heavy hydrocarbons, ...	28·1	,,
Oxygen, ...	0·2	,,
Carbonic oxide, ...	0·6	,,
Methane, ...	44·8	,,
Hydrogen, ...	20·5	,,
Nitrogen, ...	3·5	,,

Armstrong and Miller maintain that these gases contain a certain amount of acetylene, which can be detected by means of cuprous chloride. Young, and later Scheitauer,[2] investigated this pyrogenic decomposition of oils, and their conversion into gas, very carefully, and found that the decomposition takes place in two stages. In the first stage gaseous hydrocarbons of very low boiling point, and belonging to the fatty series, are formed; in the second these products tend to polymerise, in contact with the heated walls of the retort, forming cyclic compounds. The more rapidly, therefore, the gas is removed from the retort, the higher will be the proportion of hydrocarbons of low boiling point, a fact which it is of great interest to bear in mind in the case of the preparation of butadiene and its homologues, by the dry distillation of oils.

After purification these gases are compressed to 12 atmospheres, when they deposit, in the compressor, a complex liquid to which the name of gas-oil has been given, and which contains up to 35 per cent. of ethylene. After separating from it the tarry products, this oil represents about 15 per cent. of the raw material taken, 100 cubic metres of gas yielding about 10 kilos. of oil.

According to Scheitauer, this oil has the following composition:—

Benzene, ...	70	per cent.
Toluene, ...	15	,,
Higher homologues, ...	5	,,
Homologues of ethylene and butadiene,	10	,,

Butadiene is also found in the tar.

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[1] *J. Amer. C.S.*, 1894.

[2] *J. für Gas.*, 1898, 142.

The presence of this compound had been pointed out in 1886 by Armstrong and Miller, who on washing the oil-gas in bromine water had obtained a tetrabromide, melting at about 116° C., and, consequently, similar to that prepared by Caventou by the action of bromine on the products of dry distillation of amyl alcohol, or to that obtained by Prunier, by brominating Berthelot's synthetic divinyl.

The search for butadiene in gas-oils has been carried further by Grimaux and Cloëz, who published their results in their memoir, "Sur les dérivés de l'érythrène," in 1887.[1] The two French chemists, whilst investigating gas-oils, succeeded in establishing the difference between erythrene and the isomeric crotonylene with which Caventou confused it in his earlier work.

At the oil-gas works at Dresden, Hempel investigated the conditions under which this product was formed. In a number of experiments he determined, by means of the spectropyrometer, the temperature of the furnace by which the retorts were heated, and also the temperature inside the retorts. He found that the most favourable figure for the former was 1,030° C., and for the latter 970° C.

Under these conditions he obtained, per 100 kilos. of oil treated, 71 cubic metres of gas, which, when compressed to 10 atmospheres, gave 5,830 grms. of gas-oil.

On fractionation, the latter gave the following percentages :—

20° to 50° C.,	0·2 per cent.
50° to 75° C.,	2·2 ,,
75° to 80° C.,	16·5 ,,
80° to 85° C.,	20·5 ,,

The oil employed had a density of 0·894, and distilled completely between 238° and 300° C.

Under other conditions of temperature—viz., at 1,000° C. in the furnace and 740° C. in the retorts, 100 kilos. of oil gave 52 cubic metres of gas, which, when compressed at 10 atmospheres, gave 21,620 grms. of gas-oil, yielding on fractionation the following fractions :—

21° to 30° C.,	0·5 per cent.
30° to 40° C.,	0·5 ,,
40° to 50° C.,	0·3 ,,
50° to 77° C.,	1·3 ,,
77° to 80° C.,	24·8 ,,
80° to 82° C.,	23·5 ,,
82° to 95° C.,	13 ,,

At a temperature of 900° C. in the retort the yield of gas-oil obtained is lower, and the percentage passing over between 75° and 90° C. falls to 55.

The work of Grimaux and Cloëz demonstrated the absolute identity of Henninger's synthetic erythrene, obtained by reducing erythritol with formic acid, with the hydrocarbon contained in gas-oils.

We have given the main points of this investigation in describing the properties of erythrene; the identity between the two hydrocarbons was established by the observation that they yield identical bromides. The

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[1] *Bull. Soc. Chim.*, 1887, 48, 31.

butadiene of gas-oils is identical with the pyrrolylene, C_4H_6, prepared by Ciamician and Magnaghi from pyrrol. Colson's paper on the derivatives of erythritol and of compressed gas, which we have already quoted, completed the investigation of this question.

By distilling a large quantity of gas-oil, and brominating it, Colson was able to establish the fact that beyond butylene and diethylidene the major portion of gas-oils consisted of erythrene. These products, which had hitherto been utilised only as a source of benzine, and of which a great part, and just that portion which contains the butadiene, was lost, assume great importance in view of the synthesis of caoutchouc, and it may be that with such an interesting bye-product to hand, the oil-gas industry may undergo vigorous development, and that the petroleum residuals, which have been little used hitherto, may find a normal outlet.

Under these circumstances it is not easy to understand why Harries considered petroleum to be of no interest from the standpoint of rubber manufacture. It is true that he only examined the catalytic treatment of the isopentane fraction of the oils, and he declares that this method is of little interest for the preparation of isoprene, and is not susceptible of industrial application.

He seems to have entirely neglected the examination of gas-oils in drawing these hasty conclusions. His opinion does not appear to have been shared by the Elberfeld works, nor by Wasmer, who have taken out patents for the decomposition of petroleum residuals by means of contact masses and of platinum; the patent is of little value, for there are a large number of anticipations of it. In this process, the fraction distilling between 70° and 100° C. is passed over a network of platinum wires, heated electrically to redness, the apparatus used being somewhat similar to the isoprene lamp.

The erythrene produced is separated from the other hydrocarbons at the same time, either by compression, employing the classical method of isolating gas-oils, or by bromination, obtaining the crystalline tetrabromide and converting this into butadiene by means of zinc dust and alcohol. Various catalytic masses, such as nickel, copper, or silver, may be substituted for the platinum gauze.

These results are sufficient to indicate the interest attaching to oils in general from the point of view of synthetic rubber, and in particular to petroleum oils which are abundant and inexpensive. The illuminating gas produced by their destructive distillation is sufficient in itself to pay the cost of conversion, and the accompanying gas-oils, rich in erythrene, only require the application of pressure—an inexpensive process—in order to separate them.

For the methods of bromination employed hitherto in separating divinyl from the other hydrocarbons formed at the same time, it is possible to substitute chlorination, which is much more economical, and leads to the same results. We have, indeed, seen that gaseous chlorine combines very energetically with butadiene, forming a crystalline tetrachloride, $C_4H_6Cl_4$, melting at 73° C. This tetrachloride is similar to the tetrachlorhydrin of erythritol, and has the same melting point. It is decomposed when heated with alcohol and zinc, and even with metals such as iron, erythrene being formed together with the corresponding metallic chloride.

It is probable that butadiene would also be found in the natural gases which are met with in Pittsburg, Pennsylvania, Ohio, Pechelbronn, Kertsch, and the Peninsula of Apscheron; the mode of formation of these gases, and the proximity of their sources to the petroleum wells render this a very plausible hypothesis. No investigation, so far as we are aware, has been undertaken in this direction, and the old analyses of these gases tell us nothing, for since butadiene was of no particular interest at the time they were made, it was classified with the rest of the olefines and determined as such, without any special designation.

It is also probable that by washing with chlorine water, or treating with a current of chlorine gas, the volatile products arising from the purification and distillation of petroleum, large quantities of butadiene, which are now lost, might be collected.

An attempt might also be made to treat the pentane and isopentane fractions of petroleum direct. Lachowitz[1] has made some experiments in this direction with Galician petroleum. He has isolated a pentane fraction having a density of 0·6267 at 14° C. and boiling at 37° C.—

$$CH_3—CH_2—CH_2—CH_2—CH_3,$$

and isopentane boiling at 29° C.—

$$(CH_3)_2CH—CH_2—CH_3,$$

and by treating them with chlorine gas has readily obtained, in the cold, various chlorides. Isopentane forms a chloride with a density of 0·870 at 20° C. and boiling at 100° C.; it has the formula

$$(CH_3)_2CH—CH_2—CH_2Cl.$$

Pentane gives two isomeric chlorides, one boiling at 106° C. and having a density of 0·8732; the other boiling at 104° C. By the action of dry gaseous chlorine in sunlight, both these chlorides are converted into a dichloride of the formula

$$CH_3—CH_2—CH_2—CHCl—CH_2Cl.$$

It is possible that by applying to this compound the method of treatment instituted by Harries for dihaloids—that is to say, the action of soda lime at 600° C.—there would be a chance of obtaining isoprene, if the necessary molecular migrations took place.

The same worker seems to have recognised that butadiene is to be found in that portion of the petroleum which distils below 10° C.

On these points the work of Lachowitz, which is now old, ought to be repeated, especially since it was not originally carried out from the present point of view.

It is not only the destructive distillation of petroleum which may give rise to butadiene or isoprene. Lebel found that divinyl was formed when boghead coal was distilled, and it is also formed in the manufacture of illuminating gas from cannel coal.

These questions were investigated successively by David[2] in 1883 and Davis[3] in 1886.

David, by washing the gas produced in the distillation of cannel with the oil obtained—in the distillation of tar—intermediate between the phenols

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[1] *Annalen*, 1883, 220, 118.

[2] *J. Soc. Chem. Ind.*, 1883.

[3] *Ibid.*, 1886.

and the anthracene oil, obtained about 20 litres of a complex liquid per ton of coal distilled. By fractionating this product he obtained, in addition to benzene, toluene, and xylene, pentane, boiling at 37° to 39° C., amylene, butadiene, hexane, hexylene, and thiophene, all of which are interesting products from the point of view of caoutchouc synthesis. Davis used olive oil as washing liquid, and found that 10 litres of hydrocarbons, distilling between 23° and 106° C., were obtained per ton of cannel. The portion which distils below 80° C. is of interest to us; it can be fractionated as follows:—

At 23° C.,	12 per cent.
30° to 35° C.,	1·5 ,,
73° to 78° C.,	11·2 ,,
80° to 83° C.,	41·0 ,,

The study of these products of the purification of boghead and cannel gas has promise of great interest, as will be seen, and it is very desirable that it should be undertaken, with the application of the latest methods worked out for the investigation of erythrene and its homologues.

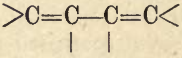
Lebedew and Skawronska[1] have recently attempted the preparation of butadiene, by heating ether vapour in presence of aluminium powder—

$$3(C_2H_5)_2O + 2Al \rightarrow Al_2O_3 + 3(CH_2 = CH - CH = CH_2) + 6H_2$$

The product is washed with bromine water and, after distilling the dibromide formed in a current of steam, it is converted into erythrene by heating with alcohol and zinc. The Bayer works[2] propose as a pyrogenic method of preparing butadiene the employment of *cyclo*-hexanes, which they decompose by the process used in the case of the *cyclo*-hexanols, to which we have already referred. Finally, Perkin, Matthews, and Strange have pointed out that ethylene hydrocarbons containing the grouping

$$>C=\underset{|}{C}-\underset{|}{C}H-CH<$$

are capable of yielding, on dry distillation, diolefines of the formula



$$>C=\underset{|}{C}-\underset{|}{C}=C<$$

by loss of hydrogen; these may form homologues of isoprene.

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[1] *J. Russ. Soc.*, 1911, 43, 1124.

[2] Ger. Pat. 248,738; Eng. Pat. 448 of 1912.

CHAPTER XIII.

METHODS OF PREPARING ISOPRENE AND ITS HOMOLOGUES.

(*Continued.*)

Methods of Group 2.—Use of Halogen and Hydroxy-Derivatives.—This group comprises reactions which have as their starting point halogen or hydroxy-derivatives of hydrocarbons, from which unsaturated hydrocarbons are obtained by the removal of the elements of a halogen acid or of water, respectively.

A large number of substances are capable of serving in this way for the preparation of hydrocarbons containing two conjugated double linkings, and thus endowed with the property of polymerising to caoutchouc; it follows that the number of processes belonging to this group is very great; most of them are, however, possessed of only laboratory value, and cannot possibly be industrialised, as much on account of the difficulty of carrying out the various reactions as of the costliness of the materials employed, which are often very difficult to recover.

It should not, in fact, be forgotten that, for a synthesis to be of interest, it is necessary to be able to produce the synthetic product at a price which is lower than that at which it can be obtained from natural products; if the cost of the synthetic product be the higher, no matter how elegant the process, nor how much labour and ingenuity have been expended upon its elaboration, the question remains untouched, and the problem has still to be solved.

Of the processes classed in this group, although many can never be applied practically, yet others, such as those worked out by Hoffmann and Coutelle, and by Perkin and Matthews, and their collaborators, as well as those starting with petroleum or calcium carbide, deserve attention, for there is some hope of their being worked up into industrial processes. In organic chemistry, since it is only rarely that reactions occur quantitatively, and it is nearly always a question of dealing with systems in equilibrium from which only a portion of the desired substance can be separated, the fewer the stages in the reaction the better will be the process. On the other hand, as we have already said, the employment of certain reagents, which is possible in the laboratory, is impracticable industrially; their price is too high and the risks of loss during the course of the operation are such that their use must be excluded. Any method which involves the use of iodine or its derivatives, bromine or its derivatives, methyl chloride, and even hydrogen gas must be regarded as doubtful; for in order to obtain a product of which the cost shall not exceed 1s. 2d. per lb., the employment of materials, worth from 2s. 6d. to 4s. 6d. per lb., which can only be recovered incompletely and with difficulty, will always be a speculative operation.

The employment of comparatively low but constant temperatures is also a fairly frequent stumbling block. It is possible to maintain a temperature of 400° C. exactly by means of a sulphur bath, but although this is a comparatively simple thing to do in the laboratory, it is not practicable on the large scale. The fact that it was necessary to do so, for instance, prevented the industrial development of the beautiful synthesis of alkali ferrocyanides, worked out by Tcherniac and Norton, starting with ammonia and carbon bisulphide. So long as the temperature does not exceed 350° C., as in the dye industry, the oil bath can be conveniently and fairly safely used, but if it be necessary to reach 600° C., as in certain reactions suggested by Harries —*e.g.*, the decomposition of the dihalogen derivatives of isopentane by means of soda lime—it is exceedingly difficult to realise a constant temperature, even by the use of fusible metal baths, and is indeed scarcely possible without using, at considerable cost, rheostats and electric current.

For these reasons, of a purely technical character, all syntheses based upon bromination or methylation, or upon decompositions or conversions at a constant temperature, seem destined in advance to encounter a deadlock on the technical side. The same is true of syntheses which start with comparatively rare substances, the price of which is necessarily too high to allow of a remunerative cost of production.

The reason for the strong position of the dye industry resides in the fact that all the syntheses comprised in it have found in coal-tar derivatives the inexpensive raw materials required.

Harries has, therefore, put the matter upon a proper basis by pointing out that the future industry of synthetic rubber should be inspired by the same principles, and should seek amongst those natural products which are abundant and inexpensive, such as tar, starchy substances, petroleum products, alcohols, and hydrocarbons, the necessary raw materials.

We shall see, later, that it seems easier to arrive economically in this way at the preparation of butadiene than of its various homologues, and that the rubber derived from this hydrocarbon is the rubber of the future, if its properties turn out to be identical with those of natural rubber. In any case the endeavour should be, in this conversion of carbon compounds, to work out reactions which are as few in number and as complete as possible; the shorter the route, the better the yield.

In his researches on isoprene Bouchardat had obtained, by the action of moist silver oxide on isoprene monohydrochloride a tertiary alcohol, in the form of a colourless liquid, with a pleasant odour, sparingly soluble in water, insoluble in amyl alcohol, and boiling between 120° and 130° C. Bouchardat regarded this compound as a hydrate of isoprene, and did not pursue its study further. It was taken up again, first by Wagner, who found that it was isomeric with ethylvinyl carbinol, obtained by the action of zinc-ethyl on acroleïn, then by Menschutkin, who gave it the formula

$$CH_2{=}C(CH_3){-}CH(OH){-}CH_3.$$

Gadziatsky[1] examined this compound, and showed that it was a tertiary alcohol; he ascribed to it the constitution of dimethylvinyl carbinol—

$$(CH_3)_2C(OH){-}CH{=}CH_2.$$

The formation of Bouchardat's alcohol must, therefore, be preceded by the isomeric change of isoprene to unsymmetrical dimethylallene—

$$\begin{aligned} CH_2{=}C(CH_3){-}CH{=}CH_2 &\rightarrow (CH_3)_2C{=}C{=}CH_2 \\ &\rightarrow (CH_3)_2C(OH){-}CH{=}CH_2. \end{aligned}$$

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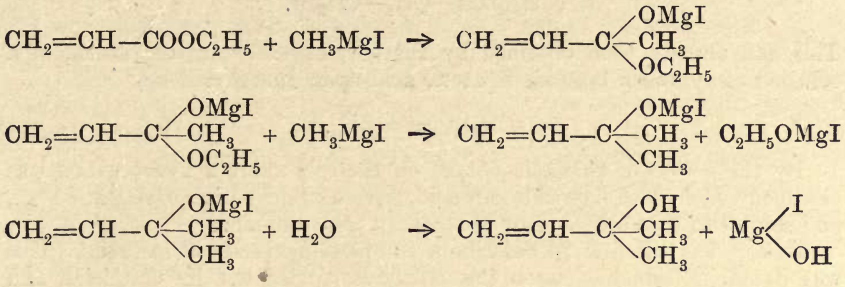
[1] *Bull. Soc. Chim.*, 1887, 48, 168.

This isomeric change can be brought about by heating isoprene with alcoholic hydrogen chloride.

The alcohol can also be prepared, according to Harries, by Grignard's reaction, using ethyl acrylate and magnesium methyl iodide, the reaction proceeding in the following stages :—



$$CH_2{=}CH{-}COOC_2H_5 + CH_3MgI \rightarrow CH_2{=}CH{-}C\left\langle\begin{matrix}OMgI\\CH_3\\OC_2H_5\end{matrix}\right.$$

$$CH_2{=}CH{-}C\left\langle\begin{matrix}OMgI\\CH_3\\OC_2H_5\end{matrix}\right. + CH_3MgI \rightarrow CH_2{=}CH{-}C\left\langle\begin{matrix}OMgI\\CH_3\\CH_3\end{matrix}\right. + C_2H_5OMgI$$

$$CH_2{=}CH{-}C\left\langle\begin{matrix}OMgI\\CH_3\\CH_3\end{matrix}\right. + H_2O \rightarrow CH_2{=}CH{-}C\left\langle\begin{matrix}OH\\CH_3\\CH_3\end{matrix}\right. + Mg\left\langle\begin{matrix}I\\OH\end{matrix}\right.$$

It would seem, then, that isoprene can be prepared starting either with dimethylallene or with dimethylvinyl carbinol.

The earliest researches seriously undertaken with a view to working out a synthesis of isoprene, were those of Kondakow, whose investigations on butadiene and its derivatives extended over many years, and to whose work is due a great deal of the progress achieved in this direction.[1] By chlorinating trimethylethylene, $(CH_3)_2C{=}CH{-}CH_3$, or *β-iso*-amylene, which he had prepared by the action of zinc chloride on amyl alcohol, he obtained an unsaturated monohydrochloride :—

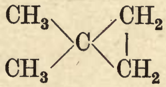
$$(CH_3)_2C{=}CH{-}CH_3 \rightarrow CH_2{=}C(CH_3){-}CHCl{-}CH_3,$$

which, when heated at 150° to 170° C. with alcoholic potash, yielded isoprene,

$$CH_2{=}C(CH_3){-}CHCl{-}CH_3 \rightarrow CH_2{=}C(CH_3){-}CH{=}CH_2.$$

The yield was about 10 grms. of isoprene for every 150 grms. of the original hydrocarbon taken, which is hardly an industrial result. The synthetic isoprene thus obtained was characterised by means of its halogen derivatives, which were found to be similar to those obtained from "pyrogenic" isoprene, and from dimethylallene. These experiments were in agreement with those of Gadziatsky, which had just been published by Wolkof (1888).

Proceeding, Kondakow, in 1889, established the fact that the dihydrochloride of isoprene, prepared by Bouchardat, was identical with the dihydrochloride of dimethylallene, and that it could also be derived from *β*-dimethyltrimethylene or dimethyl-*cyclo*-propane—



With the aid of these two compounds isoprene could, therefore, be prepared, but these syntheses, although interesting from a scientific point of view, were absolutely negligible as industrial propositions.

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[1] *J. Russ. Soc.*, 1888, 20, 706; 1889, 21, 57; 1892, 24, 513. *Rev. gen. chim. pur. et appl.*, 1912.

We may recall here the experiments of Ipatiew and Wittorf,[1] which have already been referred to in connection with the constitution of isoprene.

These authors showed that when isoprene reacts with hydrogen bromide, the dibromide of α-dimethyltrimethylene is formed,

$$\mathrm{(CH_3)_2CBr{-}CH_2{-}CH_2Br.}$$

This had already been obtained by Ipatiew, in 1897,[2] by the action of a solution of hydrogen bromide in acetic acid upon dimethylallene,

$$\mathrm{(CH_3)_2C{=}C{=}CH_2.}$$

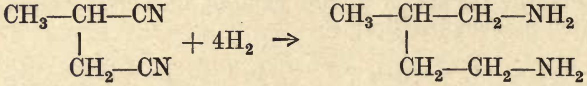
By the action of alcoholic potash on the dibromide a hydrocarbon was obtained which, with hypochlorous acid, gave a chlorhydrin melting at 81° C., and similar to that obtained by Mokiewsky from isoprene.

Euler[3] was the first to describe a complete synthesis of isoprene. This was based, in principle, upon the synthesis carried out by Ciamician and Magnaghi, in 1885, when they prepared divinyl from pyrrolidine.

When propylene dibromide is treated with potassium cyanide the dinitrile of pyrotartaric acid is formed, according to the equation

$$\mathrm{CH_3 \cdot CHBr \cdot CH_2Br + 2KCN = CH_3 \cdot CH(CN) \cdot CH_2 \cdot CN + 2KBr.}$$

This is reduced by alkali ethylate to β-methyltetramethylene diamine :—



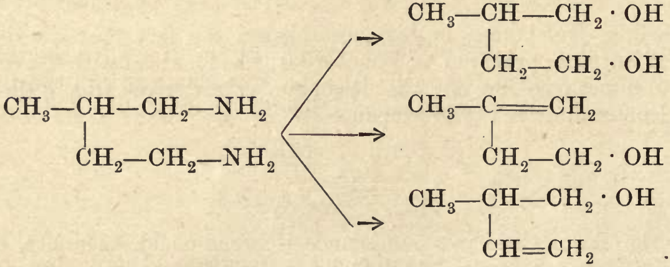
$$\begin{array}{l}\mathrm{CH_3{-}CH{-}CN} \\ \qquad | \\ \qquad \mathrm{CH_2{-}CN}\end{array} + 4\mathrm{H_2} \rightarrow \begin{array}{l}\mathrm{CH_3{-}CH{-}CH_2{-}NH_2} \\ \qquad | \\ \qquad \mathrm{CH_2{-}CH_2{-}NH_2}\end{array}$$

We shall consider, under the third group, the conversion of the latter substance into isoprene, through β-methylpyrrolidine.

In another paper[4] Euler described a process, also starting from β-methyltetramethylenediamine, which is included in the group of methods which we are now considering.

The diamine is converted into the corresponding glycol by the action of nitrous acid, according to Gustavson's method.[5]

At the same time two unsaturated alcohols are obtained together with traces of isoprene—



$$\begin{array}{l}\mathrm{CH_3{-}CH{-}CH_2{-}NH_2} \\ \qquad | \\ \qquad \mathrm{CH_2{-}CH_2{-}NH_2}\end{array} \begin{array}{l} \nearrow \begin{array}{l}\mathrm{CH_3{-}CH{-}CH_2 \cdot OH} \\ \qquad | \\ \qquad \mathrm{CH_2{-}CH_2 \cdot OH}\end{array} \\ \rightarrow \begin{array}{l}\mathrm{CH_3{-}C{=}CH_2} \\ \qquad | \\ \qquad \mathrm{CH_2{-}CH_2 \cdot OH}\end{array} \\ \searrow \begin{array}{l}\mathrm{CH_3{-}CH{-}CH_2 \cdot OH} \\ \qquad | \\ \qquad \mathrm{CH{=}CH_2}\end{array}\end{array}$$

β-methyltetramethylenediamine.

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[1] *Centralblatt*, 1900, 2, 331.

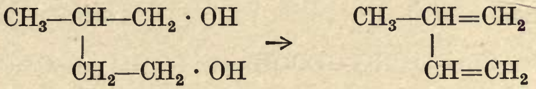
[2] *J. Russ. Soc.*, 1897, 29.

[3] *Ber.*, 1897, 30, 1989.

[4] *Ber.*, 1895, 28, 2952.

[5] *Ber.*, 1892, 25, 912.

Isoprene is readily obtained by the dehydration of β-methyltetramethylene glycol—

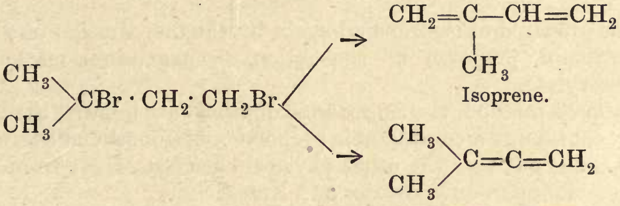


$$\begin{array}{ll}\mathrm{CH_3{-}} & \mathrm{CH{-}CH_2\cdot OH}\\ & |\\ & \mathrm{CH_2{-}CH_2\cdot OH}\end{array} \rightarrow \begin{array}{ll}\mathrm{CH_3{-}} & \mathrm{CH{=}CH_2}\\ & |\\ & \mathrm{CH{=}CH_2}\end{array}$$

This method, with modifications in its first stage, has been taken up by Harries, as we shall see shortly.

Euler's process gives practically pure isoprene, whereas the methylbutadiene obtained by Ipatiew's method is always contaminated with dimethylallene.

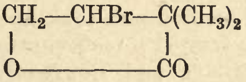
In fact, starting from the dibromide of dimethyltrimethylene, 1·3, to prepare a hydrocarbon with double bonds in the positions 1 : 3, it may be regarded as probable that the elimination of hydrogen bromide will occur in two ways, yielding, in the first place, methyl-2-butadiene 1·3, and secondly, methyl-2-butadiene, 2·3, or dimethylallene—



We have already had occasion, in a previous chapter, to refer to the physical constants of the isoprene obtained in this way. Blaise and Courtot[1] have described a method of preparing isoprene, which starts with αα-dimethyl-βγ-dibromobutyric acid—

$$\mathrm{CH_2Br{-}CHBr{-}C(CH_3)_2{-}COOH.}$$

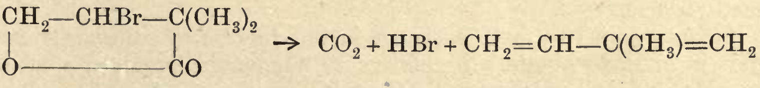
This acid yields on distillation a lactone, αα-dimethyl-β-bromo-γ-butyrolactone—



$$\begin{array}{ll}\mathrm{CH_2{-}CHBr{-}} & \mathrm{C(CH_3)_2}\\ | & |\\ \mathrm{O{-}{-}{-}{-}{-}{-}} & \mathrm{CO}\end{array}$$

which, when heated with quinoline, yields isoprene. The acid is distilled from an oil bath, and one molecule of hydrogen bromide is eliminated. The dimethylbromobutyrolactone, melting at 47° C., thus obtained is treated with three times its weight of quinoline; carbon dioxide is evolved, and isoprene, characterisable by the usual methods, is formed.

The quinoline fixes a molecule of hydrogen bromide, liberated according to the equation



$$\begin{array}{ll}\mathrm{CH_2{-}CHBr{-}} & \mathrm{C(CH_3)_2}\\ | & |\\ \mathrm{O{-}{-}{-}{-}{-}{-}} & \mathrm{CO}\end{array} \rightarrow \mathrm{CO_2 + HBr + CH_2{=}CH{-}C(CH_3){=}CH_2}$$

αα-dimethyl-β-bromo-γ-butyrolactone.

Isoprene.

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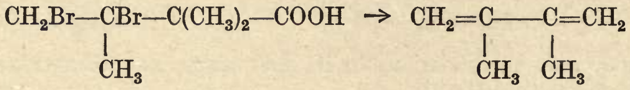
[1] *Bull. Soc. Chim.*, 1906, 35, 995.

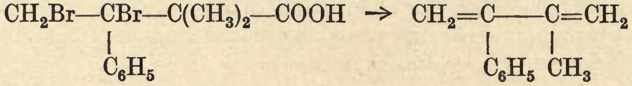
Courtot[1] obtained di-isopropenyl, by a similar reaction, from *ααβ*-trimethyl-*βγ*-dibromobutyric acid, using alkaline carbonates or pyridine in place of quinoline—



$$CH_2Br{-}\underset{\displaystyle CH_3}{\underset{|}{C}}Br{-}C(CH_3)_2{-}COOH \rightarrow CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH_2$$

It is necessary, of course, to assume that an atom of bromine changes its position during the course of the reaction.

In an analogous manner phenylisoprene was obtained by Courtot, by the action of alkaline carbonates on *αα*-dimethyl-*β*-phenyl-*βγ*-dibromobutyric acid—



$$CH_2Br{-}\underset{\displaystyle C_6H_5}{\underset{|}{C}}Br{-}C(CH_3)_2{-}COOH \rightarrow CH_2{=}\underset{\displaystyle C_6H_5}{\underset{|}{C}}{-}{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH_2$$

Finally, he prepared di-isopropenyl again by the dehydration of dimethylisopropenylcarbinol, prepared by the action of magnesium methyl iodide on ethyl metacrylate.

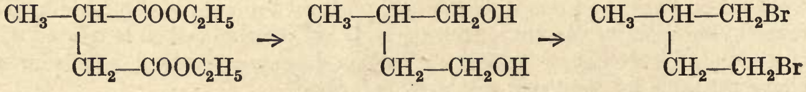
As in Ipatiew's method, the compounds obtained are impure, the isoprene, in particular, containing a considerable proportion of dimethylallene, although its boiling point is 36° C.; the other physical constants differ from those of pure isoprene, as prepared by Harries and Neresheimer.

In 1906, Harries and Neresheimer described a first method of preparing isoprene synthetically. They obtained this hydrocarbon by condensing ethyl acrylate with magnesium methyl iodide, by means of Grignard's reaction, of which we have already indicated the mechanism.

Dimethylvinylcarbinol, $(CH_3)_2C(OH){-}CH{=}CH_2$, is thus obtained, and this on dehydration yields isoprene.

Given the possibility of preparing acrylic acid fairly easily from *β*-iodopropionic acid, the method was somewhat attractive from an industrial point of view; unfortunately, the yields obtained are only small, and the products are impure.

Harries abandoned this method and took up again that of Euler, which he modified somewhat. He treated *β*-methyltetramethylene glycol, obtained from diethylpyrotartrate (Blanc and Bouveault's method[2]), with sodium and alcohol in presence of hydrogen bromide, and thus obtained a dibromide—



$$\begin{array}{l}CH_3{-}CH{-}COOC_2H_5\\ \qquad\;\;|\\ \qquad CH_2{-}COOC_2H_5\end{array} \rightarrow \begin{array}{l}CH_3{-}CH{-}CH_2OH\\ \qquad\;\;|\\ \qquad CH_2{-}CH_2OH\end{array} \rightarrow \begin{array}{l}CH_3{-}CH{-}CH_2Br\\ \qquad\;\;|\\ \qquad CH_2{-}CH_2Br\end{array}$$

By the action of quinoline hydrogen bromide is eliminated and isoprene formed, which is shown by its physical constants to be contaminated with dimethylallene.

Harries was led to make a change in this process by utilising trimethylamine in order to obtain a bisquaternary ammonium bromide, a modification which we shall consider under the third group.

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[1] Thesis, Nancy, 1705.

[2] *Bull. Soc. Chim.*, 1904, 31, 669.

Neresheimer[1] thus described the first process, which we have just analysed :—

" In a flask, fitted with a large, long, reflux condenser, 100 grms. of sodium, cut into large pieces, are placed, and a solution of 50 grms. of ethyl pyrotartrate in 200 grms. of absolute alcohol is slowly run on to it. The sodium soon melts, and is then prevented from becoming crusted over by shaking the flask.

" As soon as the reaction slows down the flask is heated in a boiling brine bath, and small quantities of absolute alcohol are added at intervals until the whole of the sodium has gone into solution.

" The greater part of the alcohol is then distilled from an oil bath, at 130° to 150° C., the flask is allowed to cool, and 200 to 300 c.c. of water is then carefully added, in order to dissolve the sodium ethylate formed. The solution is transferred to a thick-walled vessel, and a vigorous current of carbon dioxide is passed into it, in order to throw down the greatest possible quantity of sodium as carbonate. This operation takes about six hours.[2] The carbonate is separated by centrifuging and washed several times by crushing it up in a large mortar with alcohol containing a little ether. The filtrate and washings are evaporated *in vacuo* on the water bath at a temperature of 80° C., and a further large quantity of sodium carbonate is thus precipitated. The latter is washed with alcohol and ether, and all the filtrates are collected and evaporated as described above.

" The temperature is then raised, by means of an oil bath, to 125° to 130° C.; under a pressure of 12 to 13 mm. the glycol distils at 120° to 134° C., the majority passing over at 125° C. A colourless liquid is thus obtained of the consistency of glycerine, having a very characteristic odour, miscible with water and alcohol, but very sparingly soluble in ether.

" It has the elementary composition required by the formula $C_5H_{12}O_2$.

" The following figures were found for molecular refraction and dispersion :—

$d_{18^\circ} = 0{\cdot}9954$; $n_D^{18^\circ} = 1{\cdot}45173$;

$n_\alpha^{18^\circ} = 1{\cdot}44925$; $n_\gamma^{18^\circ} = 1{\cdot}41607$;

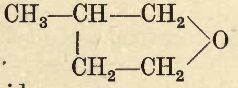
M_D, ... found = 28·20; calc. = 28·16

$M_\gamma - M_\alpha$ . . . ,, = 0·636; ,, = 0·665

The yield was 20 per cent.

" With acetic anhydride the glycol forms a diacetate, a clear liquid, with an odour of fennel, very mobile, boiling at 116° C. at 17 mm. pressure, and having the composition :—C = 57·42, H = 8·57 per cent. $C_9H_{16}O_4$ requires C = 57·36, H = 8·61 per cent. Density at 20° C. = 1·0434."

The glycol may also be characterised by converting it into β-methyltetramethylene oxide :—


$$\begin{array}{l} CH_3{-}CH{-}CH_2 \\ \quad\;\; | \qquad\quad\; \rangle O \\ \quad\; CH_2{-}CH_2 \end{array}$$

by the action of sulphuric acid.

It is a light, colourless, mobile oil, soluble in water, alcohol, and ether, and boiling at 86° to 87° C. at ordinary pressure. Its density at 18° C. is 0·8643.

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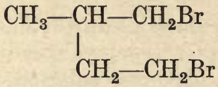
[1] Inaugural Dissertation, Kiel, 1911.

[2] *Monit. Scient.*, 1912, 26, 292.

The following may also be prepared:—(1) The symmetrical diphenyldiurethane, $C_{19}H_{25}O_4N_2$, crystallising in glistening plates, melting at 97° C., soluble in alcohol, ether, and benzene, and insoluble in water; (2) the tetraphenyldiurethane, $C_{34}H_{30}O_4N_2$, crystallising in colourless prisms, melting at 102° C., soluble in alcohol and ether and insoluble in water.

The glycol is next converted into the dibromide—



$$\begin{array}{l} CH_3—CH—CH_2Br \\ \qquad\quad | \\ \qquad\quad CH_2—CH_2Br \end{array}$$

by heating it for three hours with three times its own volume of fuming hydrobromic acid, in a sealed tube at 100° C. The product is saturated with potassium carbonate, and extracted with ether; the ether is evaporated, the residual oil dried over potassium carbonate, and fractionated under reduced pressure. The dibromide passes over at 85° to 90° C., at 12 mm. pressure. After further drying its boiling point falls to 84° C. at 11 mm.

It is a colourless, heavy liquid, with a sweetish odour; it decomposes slowly when exposed to light, hydrogen bromide being liberated.

The yield is 19 parts of bromide for every 10 parts of glycol taken.

It has the following elementary composition:—C = 26·72, H = 4·41, Br = 69·81 per cent. $C_5H_{10}Br_2$ requires C = 26·09, H = 4·38, Br = 69·13 per cent.

Its density at 17° C. is 1·6986; its molecular refraction and dispersion are as follows:—

$n_D^{17°} = 1·51217$; $n_\alpha^{17°} = 1·50918$; $n_\gamma^{17°} = 1·52722$;

M_D, ... calc. = 40·87; found = 40·13

$M_\gamma—M_\alpha$, . . . ,, = 1·25; ,, = 1·19

Neresheimer has described two methods for the conversion of the dibromide of β-methyltetramethylene into isoprene.

Method 1.—About 40 grms. of the dibromide and 150 grms. of quinoline are heated together; about 2 grms. of a very mobile liquid distils over; this is rectified over a little quinoline, and is then washed with dilute sulphuric acid, and fractionated over calcium chloride.

The isoprene distils between 30° and 37° C., and has a density of 0·678 at 19° C. The molecular refraction and dispersion were as follows:—

$n_D^{19°} = 1·41271$; $n_\alpha^{19°} = 1·40855$; $n_\gamma^{19°} = 1·43127$;

M_D, ... calc. = 24·33; found = 25·02

$M_\gamma—M_\alpha$, . . . ,, = 0·94; ,, = 1·20

M_D[1], ... ,, = 35·74; ,, = 36·82

$E_D = + 1·8$

$M_{\Sigma-\Sigma}$, ... calc. = 1·39; found = 1·77

$E_{\Sigma-\Sigma} = + 0·38$.

Method 2.—Fifteen grms. of the dibromide are heated with 25 grms. of a 33 per cent. solution of trimethylamine in absolute alcohol, for three hours in a sealed tube at 100° C.; a bisquaternary bromide is thus obtained, the further treatment of which we shall study in the third group.

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[1] Ger. Pat. 19,598.

It will be seen that the method of Harries and Neresheimer, although very ingenious, is absolutely impracticable outside the laboratory, and it has, moreover, the grave defect of giving exceedingly poor yields—20 per cent. of glycol and barely 3 per cent. of isoprene.

As it gives a practically pure product, it can be used to prepare an isoprene for comparative purposes—that is, for use as a standard—against which the purity of isoprenes prepared industrially can be compared.

Nevertheless, the method of purification by means of sulphur dioxide, suggested by the Badische Company, and to which we have referred when studying isoprene, is still simpler and more practical.

The white solid thus obtained yields, when heated, an exceedingly pure isoprene, which can be used as a standard for optical measurements. The Schering works[1] prepare isoprene by heating 2-methyl-2-3-dichlorobutane with aniline or analogous substances—

$$CH_3—C(CH_3)Cl—CHCl—CH_3 \rightarrow CH_2{=}C(CH_3)—CH{=}CH_2.$$

Butadiene is obtained by a similar reaction from 2-3-dibromobutane—

$$CH_3—CHBr—CHBr—CH_3 \rightarrow CH_2{=}CH—CH{=}CH_2.$$

This reaction is quite comparable with that which Perkin and Matthews obtain with the dichloro-derivatives of butane, and which we shall consider later on.

These same dibromo-derivatives can be converted into the corresponding unsaturated derivatives by Harries' method, which consists in heating them at 600° C. over soda lime saturated with carbon dioxide. The dibromo-derivatives themselves may be prepared in the following ways :—

(1) To obtain 2-methyl-2-3-dibromobutane—corresponding to isoprene—Grignard's reaction is made use of, acetone being condensed with ethyl bromide in presence of metallic magnesium—

$$CH_3 \cdot CO \cdot CH_3 + C_2H_5 \cdot MgBr \rightarrow (CH_3)_2C(OH) \cdot CH_2 \cdot CH_3.$$

The tertiary amyl alcohol thus formed yields, on dehydration with anhydrous oxalic acid, trimethylethylene. This hydrocarbon adds on bromine, in glacial acetic acid solution, yielding the dibromide—

$$(CH_3)_2C{=}CH—CH_3 + Br_2 \rightarrow (CH_3)_2CBr—CHBr—CH_3.$$

(2) 2-3-dibromobutane, corresponding to butadiene, may be prepared by reducing methylethylketone with sodium, and dehydrating the secondary butyl alcohol thus obtained by means of phosphoric anhydride—

$$\begin{aligned} CH_3 \cdot CO \cdot CH_2 \cdot CH_3 &\rightarrow CH_2 \cdot CH(OH) \cdot CH_2 \cdot CH_3 \\ &\rightarrow CH_3 \cdot CH{=}CH \cdot CH_3 \end{aligned}$$

In glacial acetic acid solution the hydrocarbon obtained adds on bromine.

(3) Schering,[2] again, proposed to prepare trimethylethylene by heating monochloroisopentane with an alcoholic solution of an alkali acetate at 180° C. Anhydrous lead formate, or zinc formate, may also be substituted with advantage, the reaction being more complete, and at a lower temperature.

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[1] Ger. Pat. 51,405, 52,550.

[2] Ger. Pat. 51,405, 52,550.

In connection with the methods proposed by Schering we must also mention one proposed by Ipatiew, who converts ketones and aldehydes into the corresponding alcohols, by reduction with hydrogen, in presence of iron, at 420° C.; the yield obtained is over 50 per cent., and the method could be applied in the first stage of the Schering process.

A number of methods are available for the preparation of butadiene: erythritol may be heated with formic acid, or amino-*cyclo*-butane may be methylated, as proposed by Willstätter,[1] or one may start with secondary butyl alcohol as suggested by Harries. This alcohol, as already mentioned, is prepared by reducing methylethylketone with sodium, or by the action of magnesium ethyl bromide on acetaldehyde :—

$$\mathrm{CH_3 \cdot CHO + C_2H_5 \cdot Mg \cdot Br \rightarrow CH_3 \cdot CH_2 \cdot CH(OH) \cdot CH_3 + MgBr.}$$

Commercial methylethylketone is dissolved in an equal volume of ether, and twice its volume of water is added; metallic sodium is then added, a little at a time, to the cold liquid, until a quantity equal in weight to the ketone taken has been added, and the reacting mixture is kept in constant agitation; this process takes about six hours to carry out. The upper layer is then decanted, and fractionated, using a column with glass beads, the secondary butyl alcohol being carried over with the ether; the fraction distilling between 95° and 103° C. contains the alcohol, of which a 70 per cent. yield is obtained. It is dehydrated by heating it with anhydrous oxalic acid, sulphuric acid, or, better still, anhydrous phosphoric acid, which gives a very pure butylene. The latter is condensed in a freezing mixture, dissolved in cold chloroform, and treated with a solution of bromine in chloroform until the colour of bromine persists.

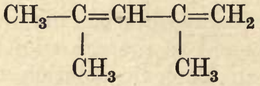
The chloroform is then distilled off under reduced pressure, and the residue fractionated; the butylene dibromide passes over at 62° C., at 11 mm. pressure.

This dibromide is converted into butadiene by heating with saturated soda lime in Harries' apparatus.

On account of the high volatility of butadiene the condenser must be cooled with solid carbon dioxide and ether, and as a certain amount of monobromide is carried over, it is well to employ two condensers in series, the monobromide remaining in the first.

The butadiene prepared in this way is rather impure; it is purified by the use of a process recommended by Thiele, which consists in converting it into tetrabromide, by adding to its chloroform solution, cooled to 0° C., a solution of bromine in chloroform, drop by drop, until a red colouration persists; but this process is slow and the yield is poor.

Grignard[2] prepared dimethyl-2-4-pentadiene-1-3, by the action of magnesium methyl iodide on ethyl dimethylacrylate :—



$$\begin{array}{ccccccccc} \mathrm{CH_3} & — & \mathrm{C} & = & \mathrm{CH} & — & \mathrm{C} & = & \mathrm{CH_2} \\ & & | & & & & | & & \\ & & \mathrm{CH_3} & & & & \mathrm{CH_3} & & \end{array}$$

This hydrocarbon contains two conjugated double linkings, and is, therefore, capable, according to Kondakow's theory, of yielding a caoutchouc by condensation.

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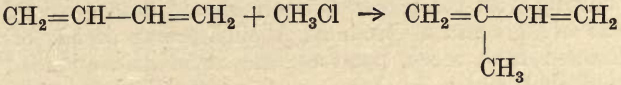
[1] *Ber.*, 1905, 28, 1992.

[2] *Compt. rend.*, 1900, 130, 1324.

Heinemann prepares isoprene by condensing methyl chloride with divinyl, or, better still, with a mixture of acetylene and ethylene, by passing them through a tube heated to dull redness :—

$$CH\equiv CH + CH_2=CH_2 \rightarrow CH_2=CH-CH=CH_2$$



$$CH_2=CH-CH=CH_2 + CH_3Cl \rightarrow CH_2=\underset{\displaystyle CH_3}{\underset{|}{C}}-CH=CH_2$$

The acetylene is produced, by preference, from calcium carbide, and the ethylene from ethyl alcohol and concentrated sulphuric acid, but Heinemann[1] points out that the preparation may be carried out starting with other suitable compounds.

The acetylene and ethylene are mixed together and heated in an iron tube or receiver at a dull red heat; divinyl is thus produced.

The latter is converted into isoprene by heating with methyl chloride, or the three gases may be mixed together and heated in an iron tube at a dull red heat.

This process, which is one of the earliest, was worked out before the possibility of condensing butadiene to a caoutchouc was known. There is no longer any necessity for the delicate and expensive methylation with methyl chloride.

As for the first part of Heinemann's process, it is taken in its entirety from Berthelot, and has been public property for fifty years. Heinemann's process, then, seems to be devoid of value; moreover, when it was published it was strongly criticised by Harries, who threw doubt upon the caoutchouc obtained by it. Nevertheless, Heinemann exhibited in London, in 1911, isoprene and caoutchouc which he maintained had been prepared by his process. Caventou[2] pointed out the possibility of preparing butadiene by the decomposition of the vapour of amyl alcohol in a red-hot tube.

$$CH_3-CH_2-CH_2-CH_2-CH_2-OH \rightarrow CH_2=CH-CH=CH_2.$$

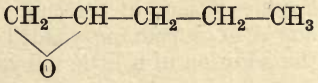
Thiele[3] repeated Caventou's experiments, and determined the amount of butadiene formed by converting it into tetrabromide; he stated that the yield was extremely small.

As we shall see later, this idea, with some modifications, was again taken up by the Bayer works.

The Hood Rubber Company, of Boston,[4] obtains erythrene by passing butyraldehyde over aluminium silicate at a temperature of 500° to 600° C., under reduced pressure :—

$$CH_3-CH_2-CH_2-CHO \rightarrow CH_2=CH-CH=CH_2.$$

Under analogous conditions valeraldehyde gives isoprene,[5] and the following oxide :—



$$\underbrace{CH_2-CH}_{O}-CH_2-CH_2-CH_3$$

yields a piperylene.[6]

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[1] Fr. Pat. 394,795, Sept. 30, 1908.

[2] *Ann. Chim. Phys.*, 1863, 127, 93.

[3] *Ibid.*, 1896, 308, 339.

[4] U.S. Pat. 1,033,327, Sept. 23, 1912.

[5] U.S. Pat. 1,033,180, Sept. 23, 1912.

[6] U.S. Pat. 1,033,179, Sept. 23, 1912.

The majority of the processes which have been referred to cannot be used industrially. Isoprene and its homologues constituting the raw material for the preparation of the best synthetic rubber, it was of the highest importance to find methods which could be applied industrially, and, during the last five or six years, very great efforts have been made in this direction.

Harries, starting with the idea that there should be a great advantage in making use of agricultural products, thought, first of all, of starchy materials extracted from seeds, potatoes, and artichokes, and had visions of using also alcohol, which, in Germany, is produced abundantly, and at a very low price.[1]

On oxidation alcohol is readily converted into acetic acid, from which acetone can be obtained; by applying the Grignard reaction to the latter, using ethyl bromide, tertiary amyl alcohol is produced, and this yields trimethylethylene,

$$(CH_3)_2C{=}CH{-}CH_3,$$

on dehydration.

Then, using an old process due to Ipatiew, the trimethylethylene is converted into pure dibromide, from which trimethylallene is obtained by the action of alcoholic potash. Trimethylallene adds on hydrogen bromide, forming a saturated dibromide—

$$(CH_3)_2CBr{-}CH_2{-}CH_2Br,$$

which when heated with alcoholic potash yields isoprene, but unfortunately the yield is very poor.

Harries[2] retained the whole of the first stage in this process, where the yields are good. He started with acetone and ethyl bromide, employing Grignard's method, and obtained an 80 per cent. yield of the carbinol; this was rectified through a column of good length, on account of its volatility in ether vapour.

When heated with anhydrous oxalic acid (half molecular proportion) or sulphuric acid, the carbinol is readily converted into ordinary amylene, or trimethylethylene, boiling at 35° C., at ordinary pressure. The yield is about 70 per cent.

In brominating, 200 parts by weight of amylene were dissolved in its own volume of acetic acid, and a solution of 450 parts of bromine in the same quantity of acetic acid was added to it slowly in the cold. The bromide was then precipitated, by the addition of water, and decanted. When dry the bromide boils at 70° C. at 30 mm. pressure; the yield is about 69 per cent. The crude amylene bromide may be dealt with direct, but a purer isoprene is obtained if it be first of all distilled.

The sequence of the processes employed by Harries differs from that of Ipatiew's method, which was followed by Harries as far as the preparation of amylene bromide.

The German chemist noticed that, in presence of strongly heated soda lime, the halogen derivatives of isopentane yielded isoprene, and that the yield was improved by the addition of a little anhydrous oxalic acid during the heating.

He also observed that the reaction went better if soda lime saturated with carbon dioxide or calcium carbonate were employed; soda lime itself

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[1] *Z. angew. Chem.*, 1907, 20, 1265.

[2] *Mon. Scient.*, 1912, 26, 295.

gave better results than calcium carbonate on account of its greater porosity.

The formation of calcium halides during the reaction had, it is true, the disadvantage of rapidly destroying the apparatus in which it was carried out, but Harries got over this difficulty in the following way :—

He had an alembic made of iron or brass, surmounted by a dome, kept in a fixed position by means of a screw. From the middle of this dome a vertical tube stood up, with a delivery tube leading from the side ; the top of the tube was fitted with a stopper through which a second metal tube passed downwards to within a few centimetres of the bottom, carrying a narrow glass tube. Through the latter the amylene dibromide was run, drop by drop, from a dropping funnel.

In the bottom of the alembic was a layer of well-dried soda lime, thoroughly saturated with carbon dioxide ; above this a wire-gauze cylinder, surrounding the tubes described above was placed, and then at some distance two other cylinders, also made of wire gauze, with an empty space between them. The space between the walls of the alembic and the cylinders was filled with soda lime.

The apparatus was then closed and heated electrically at exactly 600° C.

The amylene dibromide was then run in, drop by drop ; the white fumes given off were led through a spiral condenser and condensed in a vessel cooled to zero. From 200 parts of amylene dibromide and 300 parts of soda lime, 36 to 40 parts of isoprene boiling at 37° C. were obtained ; the yield was thus about 60 per cent.

When the dibromide is run on to soda lime which has not been previously saturated with carbon dioxide, it is found that the isoprene obtained is much less pure, being contaminated with trimethylethylene.

In another experiment Harries used the unsaturated monochloride—

$$(CH_3)_2CCl—CH=CH_2$$

instead of the dibromide ; this he obtained by the careful treatment of the carbinol—

$$(CH_3)_2C(OH)—CH=CH_2$$

with hydrogen chloride.

This chloride, in contact with non-neutralised soda lime in presence of oxalic acid, gives a 40 per cent. yield of fairly pure isoprene. From the point of view of purity, the products obtained by the use of soda lime—carbonated or not, according to the halogen employed—give far better results than those obtained by the use of quinoline, as first used by Harries, or of fused potash.

With quinoline, as we have already seen, only traces of isoprene are obtained, and much dimethylallene,

$$(CH_3)_2C=C=CH_2.$$

With potash a little more of the desired hydrocarbon is obtained, but an unsaturated bromide,

$$(CH_3)_2C=CBr—CH_3,$$

remains, from which the last molecule of hydrogen bromide cannot be removed.

By substituting methylethylketone, or butanone,

$$CH_3—CO—CH_2—CH_3,$$

for acetone Harries obtained butadiene, in the following manner :—

He took 500 parts of commercial butanone, obtained by the dry distillation of a mixture of barium propionate and barium acetate, dissolved it in its own volume of ether, added twice its volume of water, and then, gradually, 500 parts of sodium, keeping the liquid well cooled and in constant motion.

The operation lasts about six hours: the upper layer of the product consists of secondary butyl alcohol, which is decanted and fractionated, the portion passing over between 90° and 105° C. being collected separately. The yield of the alcohol,

$$CH_3—CH_2—CH(OH)—CH_3,$$

is 73 per cent. This is next dehydrated by heating it with anhydrous oxalic acid, sulphuric acid, or, preferably, phosphoric anhydride, a yield of 47 per cent. of a very pure butylene being thus obtained. This is condensed with the aid of a freezing mixture, and diluted with twice its own volume of chloroform; a solution of bromine in chloroform is then added until the colour of bromine persists, when the chloroform is distilled under reduced pressure and the residue fractionated, the portion passing over at 62° C. at 12 mm. being collected. The yield is about 60 per cent. The conversion of the butylene dibromide into butadiene is effected by means of soda lime saturated with carbon dioxide, in the apparatus already described.

On account of the high volatility of this hydrocarbon it is necessary to cool the condenser thoroughly by means of a mixture of solid carbon dioxide and ether.

The product obtained is by no means pure; it contains a large quantity of butadiene, but also some unreduced monobromide.

It is purified by Tilden's method,[1] by conversion into tetrabromide. The crude butadiene is dissolved in two volumes of well-cooled chloroform, surrounded by a freezing mixture, and a solution of bromine in chloroform is then added until the colour of bromine persists; a 22 per cent. yield of tetrabromide is thus obtained, which, on reduction by Thiele's process, yields a very pure butadiene.

When the chloroform is evaporated a large quantity of butylene dibromide remains behind, which can be again converted.

Harries also described another process for the preparation of butadiene, starting with acetaldehyde, and employing Grignard's reaction, with magnesium ethyl bromide.

Although the raw materials for these various methods can be obtained fairly advantageously, the products which have to be brought in as intermediate reagents—such as ether, chloroform, bromine—are too expensive for Harries' syntheses ever to become industrial propositions. They can only serve for the preparation, in the laboratory, of type products, for use in controlling the purity of the industrial products.

Nevertheless, the process of decomposition of the halogen derivatives by means of soda lime must be remembered, for, although the temperature of the reaction is rather difficult to maintain satisfactorily, the yields obtained are such as should be looked for in a commercial process.

Starting with diethyl ketone, $C_2H_5 \cdot CO \cdot C_2H_5$, which is readily obtained to-day, in good yield, by Senderens' method—consisting in passing propionic

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[1] *Centralblatt*, 1901, 2, 113.

acid vapour over alumina, or zinc oxide at 400° C., according to the equation—

$$\begin{array}{l} C_2H_5 \cdot COOH \\ \\ C_2H_5 \cdot COOH \end{array} \rightarrow H_2O + CO_2 + C_2H_5 \cdot CO \cdot C_2H_5,$$

—and employing the methods of Harries which have just been described, dimethylbutadiene can be prepared.

Butadiene can also be obtained by condensing vinyl chloride, $CH_2{=}CHCl$ (obtained by heating ethylene dichloride with alumina at 370° C., according to the method of Senderens) in presence of metallic sodium, according to the equation—

$$2CH_2 : CHCl + 2Na = CH_2 : CH{-}CH : CH_2 + 2NaCl.$$

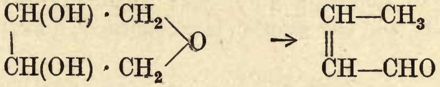
Butadiene can, again, be prepared from erythritol, which yields with formic acid—according to Henninger's method—various formins, diformin predominating.

When erythritol reacts[1] with 4 parts of formic acid (70 to 80 per cent.), says Henninger, it yields a number of formins, which decompose when heated at 210° C., forming carbon dioxide, mixed with monoxide, erythrol, butadiene, crotonic aldehyde and its isomeride, and lastly erythrane—

$$\begin{array}{l} CH(OH) \cdot CH_2 \cdot OH \\ | \\ CH(OH) \cdot CH_2 \cdot OH \end{array}$$

Erythritol.

$$\underset{\text{Erythritol diformin.}}{C_4H_6(OH)_2(O \cdot CO \cdot H)_2} = 2CO_2 + 2H_2O + \underset{\text{Butadiene.}}{CH_2 = CH{-}CH = CH_2}$$



Erythrane. Crotonic aldehyde.

The yield is extremely small—barely 2 per cent. The process, however, deserves mention, because it was the first by which butadiene—long confused with crotonylene—was obtained; but the price and scarcity of erythritol render it useless as a practical method.

Matthews and Strange[2] treat the halogen derivatives of isopentane with chlorine or bromine, afterwards removing halogen acids by means of a base. These chemists also, in collaboration with Perkin,[3] prepare isoprene in the following manner:—They condense acetone with ethyl α-bromopropionate, in presence of zinc—

$$(CH_3)_2CO + CH_3 \cdot CHBr \cdot COOC_2H_5 \rightarrow (CH_3)_2C(OH) \cdot CH(CH_3) \cdot COOC_2H_5$$

On dehydration, this ester-alcohol is converted into ethyl trimethylacrylate—

$$(CH_3)_2C : C(CH_3) \cdot COOC_2H_5,$$

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[1] *Bull. Soc. Chim.*, 19, 2135; 34, 195; 25, 225-418.

[2] Eng. Pat. 4,572, Feb. 23, 1911.

[3] Eng. Pat. 5,931, March 9, 1910.

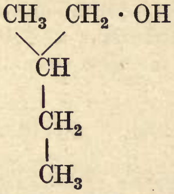
which adds on bromine, forming a dibromide—

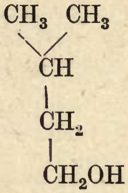
$$(CH_3)_2CBr \cdot C(CH_3)Br \cdot COOC_2H_5.$$

This dibromide yields isoprene when treated with alcoholic potash.

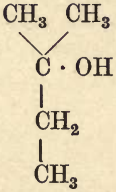
Perkin, Weizmann, Matthews, and Strange prepare isoprene, again, starting from one of the amyl alcohols, derived from isopentane.[1]

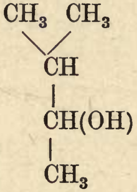
Fusel oil contains the following two alcohols :—


Active amyl alcohol.

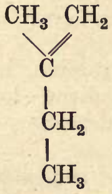

Isobutyl carbinol.

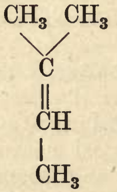
Two other alcohols derived from isopentane are also known, viz. :—

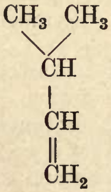

Dimethylethyl carbinol.


Methylisopropyl carbinol.

One of these derivatives (or a mixture of them), is converted by dehydration into one (or several) of the following amylenes; the dehydration is effected by means of zinc chloride, and the reaction is accelerated, if necessary, by heating :—


β-amylene.


γ-isoamylene.


α-isoamylene.

From these amylenes the dibromides or dichlorides are prepared by the action of the corresponding halogen, and these halogen derivatives when treated with alcoholic potash, sodium ethylate, or caustic soda lose HBr or HCl, yielding isoprene.

Another process, based upon the conversion of isopropenyl alcohol, has been patented by Matthews and Strange.[1] This consists in preparing isopropenyl alcohol, or its halogen derivative, by means of acetone or β-dichloropropane and ethylene; the latter may be either prepared separately, or

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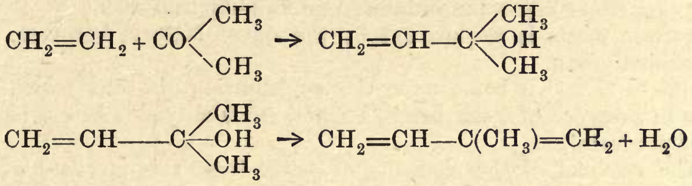
[1] Fr. Pat. 427,286, March 7, 1911.

[2] Eng. Pat. 29,566 of 1909.

formed *in situ* by the union of acetylene and hydrogen in presence of a catalyst.

In the first case water is eliminated, in the second case hydrogen chloride.

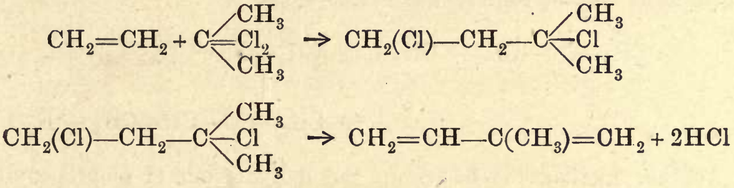
In this synthesis the following reactions are involved. Either—



$$CH_2{=}CH_2 + CO\begin{matrix}CH_3\\ \\CH_3\end{matrix} \rightarrow CH_2{=}CH{-}C\begin{matrix}CH_3\\OH\\CH_3\end{matrix}$$

$$CH_2{=}CH{-}C\begin{matrix}CH_3\\OH\\CH_3\end{matrix} \rightarrow CH_2{=}CH{-}C(CH_3){=}CH_2 + H_2O$$

or—



$$CH_2{=}CH_2 + C\begin{matrix}CH_3\\Cl_2\\CH_3\end{matrix} \rightarrow CH_2(Cl){-}CH_2{-}C\begin{matrix}CH_3\\Cl\\CH_3\end{matrix}$$

$$CH_2(Cl){-}CH_2{-}C\begin{matrix}CH_3\\Cl\\CH_3\end{matrix} \rightarrow CH_2{=}CH{-}C(CH_3){=}CH_2 + 2HCl$$

This reaction is much more complex than the preceding ones, and the isoprene obtained by it is less pure, for, in the various stages, dimethylallene is formed, together with reduction products. Perkin,[1] finally, proposed to prepare isoprene by the removal of two molecules of halogen acid from dihalogen paraffins.

These various patents, although for the most part inapplicable to industrial conditions, are highly interesting, because they constitute the starting point for what has been termed the *English synthesis*, a method which we shall consider later, and which is based upon the employment of the higher alcohols and aldehydes, derivatives of the various polysaccharides, and particularly of starch.

This is a return to the ideas which Harries [2] put forward, in 1905, in his lecture before the Chemical Society of Dantzig, when, convinced that caoutchouc is derived in nature from the sugars and pentosans, he proposed to take either starch or wood cellulose as his starting material.

Heinemann [3] had already entered upon this path, endeavouring to make use of cellulose, and of the hexoses derived from it, by converting them into levulinic acid.

Amongst patents of theoretical interest it is necessary to mention the method derived from Sawitsch's process, in which butadiene is obtained by the action of alcoholic soda on butylene dibromide.

Amongst the freak methods, we may mention that of Blum and Carpentier, who claim to obtain isoprene and butadiene by the fermentation of peat at 60° C., in presence of calcium carbonate, and a nitrogen derivative of irone. The reaction takes three weeks to complete, according to the authors, and the isoprene is obtained in a mucilaginous form (?).

The work of Hoffmann and Coutelle, chemists of the Elberfeld colour works—formerly the Bayer factory—brought the synthesis of caoutchouc,

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[1] Eng. Pat. 6,903 of 1912; Fr. Pat. 429,225 of 1912.

[2] *Z. angew. Chem.*, 1905, 20, 1203. [3] *Annalen*, 1911, 383, 164.

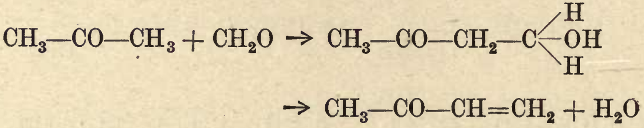
which had until then been almost exclusively of scientific interest, into the domain of industry, and they were the first to produce synthetic rubber in the factory.

We shall study most of their methods in the third group, and more particularly those relating to the use of paracresol and phenol, from which they prepare isoprene and butadiene on an industrial scale.

Certain methods worked out by the Bayer factory, however, belong to the second group.

One of these[1] is based upon the condensation of acetone with formaldehyde in presence of weak bases, a reaction which yields keto-2-butanol and other products.

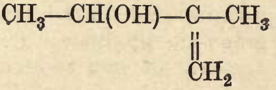
The removal of the elements of water from this alcohol-ketone yields methyleneacetone, which is then converted into isoprene. The reactions which occur may be represented as follows :—



$$CH_3—CO—CH_3 + CH_2O \rightarrow CH_3—CO—CH_2—C\begin{cases}H\\OH\\H\end{cases}$$

$$\rightarrow CH_3—CO—CH{=}CH_2 + H_2O$$

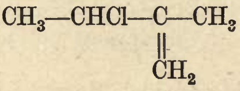
Another method[2] is based on the dehydration of isopropenylmethylcarbinol, or Bouchardat's isopropenylalcohol—



$$CH_3—CH(OH)—\underset{\underset{CH_2}{\|}}{C}—CH_3$$

by means of mineral acids, zinc chloride, oxalic acid, or sodium bisulphate It is somewhat similar to Caventou's process.

The halogen derivative of this alcohol—



$$CH_3—CHCl—\underset{\underset{CH_2}{\|}}{C}—CH_3$$

may also be treated with alcoholic potash, quinoline, aniline, or better still, with soda lime, by Harries' method.

These processes, although patented by Bayer, seem to have been very definitely foreshadowed by Kondakow[3] in his papers on isopropenyl alcohol; in these there is an undoubted anticipation of the patent, and it is strange that this was not revealed by the German Patent Office. After the publicity given to them by Kondakow as early as 1886, they may be regarded as public property.

Methylisoprene may be prepared by similar means, starting with dimethylisopropylcarbinol. Besides these processes, attempts have been made to prepare butadiene and its derivatives, starting with isopentane, obtained from petroleum distillates.

Harries states that he did not obtain any satisfactory result with these compounds, and he regards the products as devoid of interest.[4]

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[1] Ger. Pat. 222,623 of 1910. [2] Eng. Pat. 973, March 1, 1911.

[3] *J. Russ. Phys. Chem. Soc.*, 1886, 20, 706; *Jahresbuch*, 1899, 1, 880; *Centralblatt*, 1890, 1, 316.

[4] *Annalen*, 1911, 383, 157.

Kondakow[1] says that processes based upon the oxidation of these compounds have not yet been published, and that they are not known in detail. What is certain, as we shall see when we come to examine the methods of group three, is that adipic acid can readily be obtained by oxidising the compounds in question with nitric acid, and that in this way butadiene can be prepared in a way at least as economical as by starting with phenol.

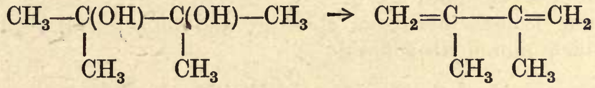
A large amount of very interesting work has been done on these lines by the group of English chemists who have studied the synthesis of caoutchouc, under the direction of Perkin, Matthews, and Strange.

On this subject, without going into the details of the results obtained, Perkin says[2] :—"Light petroleum appears to be a favourable raw material, as its production is almost unlimited. We have carried out a large number of experiments on the fixation of halogens by hydrocarbons, such as pentane and isopentane, and on the elimination of the elements of the halogen acids from these compounds. The results obtained are, in many respects, similar to those obtained with the higher alcohols."

It is certain that, by the action of chlorine, the isopentanes obtained from petroleum yield halogen derivatives, the reaction being exceedingly vigorous, and in sunlight even explosive.

By the action of metallic oxides, sodium acetate, quinoline, or soda lime, these derivatives can be deprived of one or two molecules of halogen hydride. The question is, therefore, an exceedingly interesting one to study, for petroleum is a raw material at once abundant and cheap.

Couturier[3] obtained β-γ-dimethylbutadiene or methylisoprene in 1880 by heating pinacone with sulphuric acid or acetic anhydride—

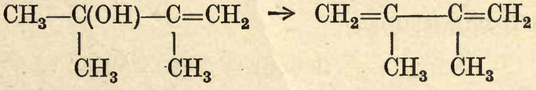


$$CH_3{-}\underset{CH_3}{\underset{|}{C}}(OH){-}\underset{CH_3}{\underset{|}{C}}(OH){-}CH_3 \rightarrow CH_2{=}\underset{CH_3}{\underset{|}{C}}{-}\underset{CH_3}{\underset{|}{C}}{=}CH_2$$

On treating tetramethylethylene dibromide with alcoholic potash, he obtained tetramethylethylene and not β-γ-dimethylbutadiene.

Solonia[4] obtained a similar negative result, using phenates.

Marintza[5] obtained β-γ-dimethylbutadiene, by the action of concentrated sulphuric or hydrochloric acid on dimethylisopropenyl carbinol in the cold, or by the action of the same acids in dilute solution (0·1 to 10 per cent.) at 50° to 100° C.



$$CH_3{-}\underset{CH_3}{\underset{|}{C}}(OH){-}\underset{CH_3}{\underset{|}{C}}{=}CH_2 \rightarrow CH_2{=}\underset{CH_3}{\underset{|}{C}}{-}\underset{CH_3}{\underset{|}{C}}{=}CH_2$$

Kondakow,[6] who was the first to attempt the condensation of dimethylbutadiene, and who succeeded in polymerising it in 1901, studied the preparation of this compound in a very special manner. He found that dimethylbutadiene was formed by the action of sulphuric acid on pinacone.

Carrying on Couturier's experiments, he obtained, by the action of alcoholic potash on the bromide and chloride of tetramethylethylene, dimethyl-

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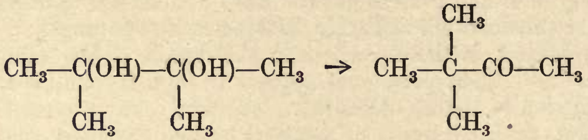
[1] *Revue de Chem. pure et appl.*, 1912 (October).
[2] *Monit. Scient.*, 1912, 26, 740.
[3] *Bull. Soc. Chim.*, 1880, 33, 454.
[4] *J. Russ. Soc.*, 1899, 30, 832.
[5] *Ibid.*, 1889, 21, 434.
[6] *J. f. prakt. Ch.*, 1899, 59, 293.

butadiene (di-isopropenyl) mixed only, in certain cases, with tetramethylethylene.

Kondakow observed that the yield of dimethylbutadiene is larger when pinacone dihydrochloride is used as the raw material, instead of pinacone itself.

The latter, in fact, always undergoes partial conversion into pinacoline, under the influence of acids, according to the equation—



$$CH_3—\underset{\displaystyle CH_3}{\underset{|}{C}}(OH)—\underset{\displaystyle CH_3}{\underset{|}{C}}(OH)—CH_3 \rightarrow CH_3—\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}—CO—CH_3 .$$

Kondakow prepares the dihydrochloride of pinacone by passing a current of dry hydrogen chloride into pinacone, in the cold.

He converts this dihydrochloride into dimethylbutadiene by heating it with alcoholic potash in a sealed tube.[1]

Harries modified Kondakow's method, which he criticises as giving too small a yield.

He dissolves anhydrous pinacone in twice its volume of chloroform, and then, whilst cooling it strongly, he passes into the solution a slow current of dry, cold, hydrogen chloride; after an hour saturation is complete, and a white mass is precipitated. The yield is almost quantitative.

The compound thus obtained is washed rapidly with ether, and placed in a desiccator, where it liquefies and volatilises readily.

It decomposes at about 55° C.

On drying it loses hydrogen chloride, and pinacone is regenerated; it appears to be a monohydrochloride—

$$(CH_3)_2C(OH)—C(OH)(CH_3)_2 + HCl.$$

When it is treated with soda lime, saturated with carbon dioxide, in the apparatus which has already been described, appreciable quantities of dimethylbutadiene are obtained.

The boiling point of this product, when distilled over sodium, is 71° C.

Its other physical constants are :—

$$d_{4^\circ}^{16^\circ} = 0{\cdot}7304, \quad n_D^{16{\cdot}5^\circ} = 1{\cdot}44321, \quad n_\alpha^{16{\cdot}5^\circ} = 1{\cdot}43870, \quad n_\gamma^{16{\cdot}5^\circ} = 1{\cdot}46303.$$

The molecular refraction is—

M_D, . . . (found) = 29·83; (calc.) = 28·93
$M_\alpha - M_\gamma$, . . („) = 1·41; („) = 1·054

Kondakow states that the methylisoprene obtained in this, as well as that prepared by his alcoholic potash process, or by the action of phenates, is by no means pure; its boiling point is too high, and there are indications of the presence of tetramethylethylene or a trimethylene hydrocarbon. The methods used in practice in order to pass from pinacone to dimethylbutadiene are based upon the methods of Couturier or of Kondakow.

The Meisenburget Delbruck process, patented by the Bayer works,[2] con-

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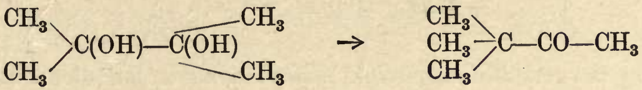
[1] *J. f. prakt. Ch.*, 1900, 62, 169.

[2] Ger. Pat. 29,350.

sists in passing pinacone vapour over sodium or potassium bisulphate, heated at 140° to 150° C.; the proportions used are 500 parts of pinacone per 750 parts of the bisulphate.

The bisulphates may also be replaced by pyrosulphates. Pinacone hydrate and a little pinacoline are formed at the same time as the dimethylbutadiene.



$$(CH_3)_2C(OH)—C(OH)(CH_3)_2 \rightarrow (CH_3)_3C—CO—CH_3$$

The hydrocarbon is dried and purified by distillation; it boils at 68° to 69° C.

Bayer[1] has also patented the preparation of dimethylbutadiene by heating pinacone at 140° C. in contact with sulphates having an acid reaction, such as chrome alum, ordinary alum, iron alum, copper sulphate, and aluminium sulphate.

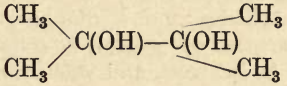
The Badische Company[2] distil pinacone or pinacoline in presence of alumina or other catalytic substance heated to 400°; they obtain a yield of 70 per cent. of hydrocarbon boiling at 69° C.

Like isoprene, methylisoprene combines with sulphur dioxide to form a solid compound, which can be resolved into its constituents again by heating; this fact may be taken advantage of for the purification of the hydrocarbon.

In view of the importance which, it would appear, must attach to dimethylbutadiene, as the raw material of synthetic caoutchouc, pinacone, from which it is prepared, has acquired a corresponding interest.

This compound has been devoid of technical interest till now, and the study of its practical preparation has hardly been begun.

Pinacone, or tetramethylethylene glycol—



$$(CH_3)_2C(OH)—C(OH)(CH_3)_2$$

is a bi-tertiary glycol, formed by the reduction of acetone, according to the equation—

$$2CH_3 \cdot CO \cdot CH_3 + H_2 = (CH_3)_2C(OH)—C(OH)\,(CH_3)_2.$$

It may be prepared by Friedel and Silva's method, as follows:—

Acetone (600 to 700 parts) is poured on to a concentrated aqueous solution of potassium carbonate, and metallic sodium (200 to 250 parts) is added in small fragments. The upper layer is fractionated, and from it are obtained isopropyl alcohol and 60 to 70 parts of pinacone, boiling at 172°.

Thiele[3] has outlined a slightly different process:—100 c.c. of acetone is floated on 150 c.c. of 30 per cent. caustic potash solution, and 28 grms. of sodium are added gradually; the liquid is, when the action of the sodium slackens, carefully diluted with water.

The fraction passing over between 150° and 180° C., when the supernatant oil is rectified, is washed with a little petroleum ether; it leaves a residue of pure pinacone.

On shaking up the petroleum ether with a small quantity of water, the dissolved portion of the pinacone is obtained in the form of pure pinacone

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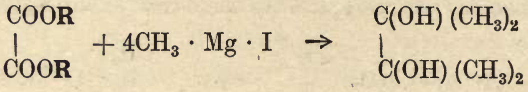
[1] Ger. Pat. 250,086.

[2] Ger. Pats. 235,311, 12,210.

[3] *Ber.*, 1894, 27, 455.

hydrate, $C_6H_{14}O_{27}6H_2O$. The yield is about 110 grms. of pinacone per kilo. of acetone.

Pinacone may also be obtained by the action of magnesium methyl iodide on oxalic ester,[1] according to the formulæ—



$$\begin{array}{l} COOR \\ | \\ COOR \end{array} + 4CH_3 \cdot Mg \cdot I \rightarrow \begin{array}{l} C(OH)\,(CH_3)_2 \\ | \\ C(OH)\,(CH_3)_2 \end{array}$$

or again by the action of magnesium methyl iodide on butadione, 2·3—[2]

$$CH_3 \cdot CO \cdot CO \cdot CH_3 + 2CH_3 \cdot Mg \cdot I \rightarrow (CH_3)_2C(OH)—C(OH)(CH_3)_2.$$

Pinacone crystallises in quadratic plates, melting at 36° C., and forms a hydrate, containing six molecules of water, and melting at about 40° C. The processes referred to above are not of much value industrially, neither is that of Fittig and Stædeler.[3]

Couturier and Meunier[4] succeeded in reducing acetone, with a view to the preparation of pinacone, by means of magnesium amalgam. The pinacone is then obtained in the form of a dry pulverulent mass, consisting of a mixture of the anhydrous substance and the hydrate. Holleman[5] modified this process; whereas Couturier and Meunier reduced acetone by means of an amalgam prepared beforehand, by a chemical method, Holleman produced his amalgam electrolytically, and caused it to act upon the acetone whilst in a nascent state, thus obtaining considerable yields with great rapidity.

The reaction is still further facilitated by the addition of a small quantity of mercuric chloride.

The requisite magnesium amalgam can be easily obtained by the electrolysis of a solution of magnesium chloride in the apparatus of Hermite and Dubosc, with mercury cathodes and a diaphragm of carbon disulphide, which serves for the preparation of electrolytic soda.

The water is replaced by acetone, and when the mercury has been freed from the magnesia formed and purified, it can be used again in the circuit.

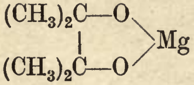
Couturier and Meunier's process has been still further improved by Richard and Langlais[6] in the following way:—

A mixture of magnesium with fifteen times its weight of mercury, dried by shaking with concentrated sulphuric acid, is heated over a naked flame and kept agitated. When quite fluid the apparatus is carefully corked, and allowed to stand for some hours, the reaction going on slowly in the cold.

On to this amalgam commercial acetone is poured. The reaction begins with the disaggregation of the amalgam, and much heat is evolved.

After cooling down the mixture a further quantity of acetone is added. The temperature gradually falls; further additions of acetone are made, and finally the apparatus is heated for one or two hours on the water bath.

Two molecules of acetone become linked up through an atom of magnesium, forming a compound—



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[1] Valeur, *Comptes rendus*, 1901, 132, 833.

[2] Zelinsky, *Ber.*, 1902, 35, 2138.

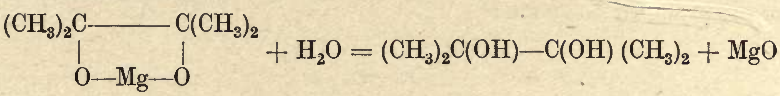
[3] Ger. Pat. 59,862; *Bull. Soc. Chim.*, 1878, 19, 98.

[4] *Annalen*, 1879, 196, 127.

[5] *Rec. trav.-chim. Pays-Bas*, 1906, 25, 206.

[6] *Bull. Soc. Chim.*, 1910, 454.

which is readily decomposed by a small quantity of water at the boiling point, yielding pinacone—



$$\begin{array}{l}(CH_3)_2C\text{———}C(CH_3)_2\\ \qquad |\qquad\qquad |\\ \qquad O\text{—}Mg\text{—}O\end{array} + H_2O = (CH_3)_2C(OH)\text{—}C(OH)\,(CH_3)_2 + MgO$$

The residual magnesia is obtained in the form of a powder which can be readily separated from the pinacone by filtration. It retains, however, a certain amount of pinacone which is extracted from it by washing with acetone, and recovered from the latter by fractionation, the acetone being used again in the process.

On adding a little water to the liquid in the reaction vessel, magnificent plates of pinacone hydrate are deposited on cooling; these crystals are washed with water, and with benzene, and finally dried. They melt at 40·5° C. The mother liquor is collected and treated as described later.

The magnesia is dissolved in sulphuric acid, when the mercury and surplus acetone separate, the former falling to the bottom of the vessel, whilst the latter floats on the solution, and can be drawn off and used again in the process.

The yield is about 70 per cent. of the quantity theoretically possible from the equation—

$$Mg+2(CH_3 \cdot CO \cdot CH_3)+7H_2O=(CH_3)_2C(OH) \cdot C(OH)(CH_3)_2,\ 6H_2O+MgO.$$

Richard and Langlais, again, have described another method for the preparation of pinacone, which is more rapid, although it gives a poorer yield—viz., not more than 60 per cent. The magnesium amalgam is prepared and the whole of the necessary amount of acetone is added to it at once, whilst the mixture is vigorously agitated; in three-quarters of an hour on the water bath the reaction is complete. The magnesium compound is then decomposed with water, and the whole heated to boiling point for a quarter of an hour.

The excess of acetone is then decanted, the residue neutralised with sulphuric acid, and distilled in a current of steam in order to remove the last traces of acetone and mesityl oxide. Water is then added to the residue, and pinacone hydrate crystallises out in plates. The wet acetone is fractionated, all that passes over up to 60° C. being collected.

Between 115° and 145° C. mesityl oxide and a little isophorone distil over. The mother liquor from the crystalline hydrate contains acetone oils, which have been examined by Bouveault and Locquin; they contain mesityl oxide, isophorone, a “diol” isomeric with pinacone, and a “triol,” together with traces of isopropyl alcohol.

Richard and Langlais' methods seem to be slower than Hollemann's, particularly if, in the latter case, electrolytically-prepared magnesium amalgam be employed. In conclusion, we may refer to two American patents taken out by the Bayer works,[1] the object of which is the preparation of pinacone.

In the first of these acetone is treated with magnesium amalgam in presence of an aromatic hydrocarbon, which behaves as an inactive vehicle, and the organo-magnesium compound produced is then decomposed. In the second, acetone is allowed to interact with mercuric chloride and magnesium in presence of toluene.

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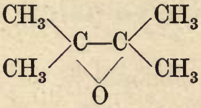
[1] U.S. Pat. 1,039,740, October 1, 1912.

The Hood Rubber Company, of Boston, Mass.,[1] have patented a process for the preparation of β-γ-dimethylbutadiene, which consists in passing the vapour of the compound—



under pressure, over aluminium silicate at 500° to 600° C.

All these processes, which have as their object the preparation of β-γ-dimethylbutadiene, with pinacone as an intermediate product, have acetone as their starting point. This compound, therefore, becomes a raw material of the greatest importance. But at present it is a comparatively unimportant by-product of the destructive distillation of wood; its total world production does not exceed 3,500 tons, and it is in great demand for the manufacture of chloroform, and as a solvent for various varnishes.

If it should come into favour as a source of caoutchouc it would be necessary to find some other source than the distillation of wood. We shall see presently that Fernbach, by subjecting starchy material to the action of a particular bacterium, has succeeded in converting it either into fusel oil, or into acetone, and that he obtains very good yields.

There are also now other sources of acetone than the Fernbach process. We shall see, presently, that, taking advantage of the catalytic activity of mercury salts, it is possible to bring about the combination of acetylene, obtained from calcium carbide, with a molecular proportion of water, and thus to obtain acetaldehyde. By oxidation—electrolytic or chemical—this aldehyde is converted into acetic acid, a process which is at present in use industrially for the preparation of the latter. In this way, therefore, an almost unlimited supply of acetone is obtainable.

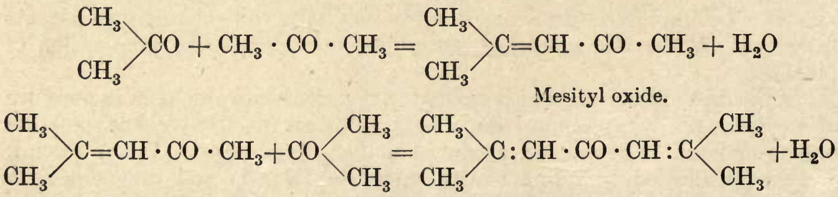
Senderens has described a method which permits of the conversion of acetic acid into acetone with an almost quantitative yield. The method consists in passing the vapour of acetic acid over alumina at 350° to 400° C. The alumina functions as a dehydrating agent—

$$2(CH_3\cdot COOH) \rightarrow CH_3\cdot CO\cdot CH_3 + CO_2 + H_2O.$$

Evolution of carbon dioxide begins at about 350° C., and traces of monoxide and of ethylene are also formed.

The liquid coming from the condenser is free from acetic acid, containing only acetone and water.

The passage of the vapour should be fairly rapid, for the acetone when once formed is readily condensed, to form mesityl oxide and phorone, according to the equations—



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CO + CH_3\cdot CO\cdot CH_3 = \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C{=}CH\cdot CO\cdot CH_3 + H_2O$$

Mesityl oxide.

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C{=}CH\cdot CO\cdot CH_3 + CO\!<\!\begin{matrix}CH_3\\CH_3\end{matrix} = \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C:CH\cdot CO\cdot CH:C\!<\!\begin{matrix}CH_3\\CH_3\end{matrix} + H_2O$$

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[1] U.S. Pat. 1,033,228, July 23, 1912.

Ethyl acetate also yields acetone when treated in the same way as acetic acid, by passage of its vapour over alumina at 360° C.—

$$2(CH_3 \cdot COOC_2H_5) = CH_3 \cdot CO \cdot CH_3 + 2C_2H_4 + H_2O + CO_2.$$

The ethylene produced is collected and employed for other purposes.

This second method, although interesting from a scientific point of view, is not adapted for industrial use on account of the high price of ethyl acetate.

Alumina behaves in these two cases as an excellent catalyst, but only provided that it has not been calcined at too high a temperature. Senderens recommends the use of alumina which has been obtained by precipitation, from a solution of sodium aluminate by means of sulphuric acid, washed thoroughly, and dehydrated by heating below a red heat.

Side by side with the work done in Germany, which led Hoffmann and Coutelle to the first syntheses of caoutchouc, Graham, Matthews, and Strange had been carrying on a series of researches in England with the same object.

Perkin, whose work on the synthesis of the terpenes designated him for such an investigation, soon joined these workers, a certain number of whose processes we have already quoted.

Matthews first of all took acetone as a starting point for the production of isoprene, then the higher alcohols separated from fusel oil. Perkin had directed his efforts towards glycerine, but this he soon abandoned.

This first group of research chemists subsequently attracted a number of collaborators. Ramsay, Tilden, and Fernbach became connected with it, and the collection of processes which to-day bears the name of the "English synthesis" is due to the work of the following chemists and bacteriologists:—Bliss, Davies, Elder, Fernbach, Kane, Matthews, Perkin, Pim, Pope, Ramsay, Schœn, Strange, Weizmann, and Wilbraham.

After having recognised the fact that the decomposition of turpentine, by destructive distillation, could not lead to an abundant and cheap supply of the raw material, reasoning from the possibility—almost the certainty—of a fall in the price of rubber to 1s. 2d. per lb., these chemists thought that the only substances from which the raw materials of synthetic rubber could be advantageously produced were wood, starch, sugar, coal-tar, or petroleum. The preparation of dimethylbutadiene from acetone obtained from wood under the conditions which we have just explained showed, moreover, that this reasoning was sound. In the case of coal-tar, Hoffmann and Coutelle were able to prepare butadiene and isoprene from phenol and cresol, constituents of coal-tar distillate.

In the case of petroleum, it is likewise possible to prepare butadiene and its homologues, either by converting it, by oxidation, into adipic and methyladipic acids, or by halogenating the isopentanes which can be separated from it.

Lastly, in the case of starchy material, obtained from the seeds of cereals or from potatoes, it is possible to prepare butadiene and its homologues by first producing the higher alcohols by fermentation, and then halogenating. Matthews and his colleagues first directed their energies upon lactic acid, $CH_3 \cdot CH(OH) \cdot COOH$, which can be readily and cheaply obtained by the fermentation of starch.

This they converted into ethyl α-bromopropionate, which on condensation with acetone, in presence of zinc, followed by dehydration, bromination, and treatment with alcoholic potash, gave them isoprene.

This constitutes the substance of the English patent of March 9th, 1910, which we have already described.

Instead of having recourse to lactic acid for the preparation of ethyl α-bromopropionate, it is much simpler to form this ethereal salt direct from propionic acid, which is produced industrially to-day in any desired quantity.

Effront has, in fact, worked out a fermentation process in which propionic acid, together with butyric acid and ammonia, is produced by the action of a specific enzyme, amydase, upon the vinasse residuals of the distillery, the amino-acids of which, such as leucin, isoleucin, etc., are split up by it.

This is a source of raw material, cheap and abundant, which does not appear to have been known to the chemists of the Perkin-Matthews group.

The first method of preparing isoprene, starting from lactic acid, is very complicated, and, on the admission of Perkin himself, the great drawback in the case of lactic acid is that its molecule contains an insufficient number of carbon atoms to yield a product containing conjugated double linkings in its molecule.

It is, therefore, necessary to join on to it, synthetically, additional carbon atoms, and this makes the process tedious and expensive.

The higher alcohols, essential constituents of fusel oil, are of greater interest from this point of view, and it is also possible to work out a method for the preparation of isoprene and its lower and higher homologues from them.

Such a result can be obtained with isoamyl alcohol, for instance.

This alcohol is obtained by fractionating fusel oil, collecting the portion distilling between 128° and 131° C., which contains 87 per cent. of isoamyl alcohol, $(CH_3)_2CH \cdot CH_2 \cdot CH_2 \cdot OH$, and 13 per cent. of active amyl alcohol, $(CH_3)(C_2H_5)CH \cdot CH_2 \cdot OH$. This mixture of alcohols is converted into amyl chlorides by passing a current of dry hydrogen chloride through it whilst heated in an oil bath. After separating the water formed in the reaction the crude amyl chloride is fractionated, all but the fraction boiling between 97° and 101° C. being rejected.

The next stage consists in converting the amyl monochloride into dichloride, an operation requiring great care if the formation of higher chlorides is to be avoided.

The difficulty has been surmounted by the employment of an apparatus designed by Pim, the essentials of which are as follows :—

The amyl chloride is kept boiling in a lower flask, its vapour passing into an upper glass globe, fitted with a condenser, and into which a current of dry chlorine is passed. The whole apparatus is exposed to sunlight, or to the light of a mercury vapour lamp, the ultra-violet radiation greatly facilitating the reaction.

Since isoamylchloride boils at a lower temperature than the dichloride, it is clear that the temperature of the condenser can be regulated in such a way that the latter falls back as it is formed into the boiling flask. The colour of the drops enables the progress of the operation to be readily followed : if they are coloured yellow, there is an excess of chlorine.

When chlorination is sufficiently advanced, a point which will be indicated by the thermometers, the product is fractionally distilled, and the unchanged isoamyl chloride separated from the mixture of isomeric dichlorides, boiling, approximately, at 140° to 175° C.

The following constituents can be separated:—

1. Isopropylethylene dichloride,
   $(CH_3)_2CH \cdot CHCl \cdot CH_2 \cdot Cl$, boiling point 142° C.
2. Dimethyltrimethylene dichloride,
   $(CH_3)_2CCl \cdot CH_2 \cdot CH_2Cl$, boiling point 152° C.
3. β-methyltetramethylene dichloride,
   $CH_2Cl \cdot CH(CH_3) \cdot CH_2 \cdot CH_2Cl$, boiling point 170° C.

The constitution of isopropylethylene dichloride is demonstrated by the fact that on heating it with soda lime isopropylacetylene is obtained—

$$(CH_3)_2CH \cdot CHCl \cdot CH_2Cl \rightarrow (CH_3)_2CH \cdot C \vdots CH,$$

together with a little isoprene, resulting, as is frequently the case, from intramolecular change. Isopropylacetylene is characterised by its reaction with copper and silver salts, and by its conversion into methylisopropylketone, boiling at 96° C., by the action of a mercuric salt.

Dimethyltrimethylene dichloride forms the chief constituent of the chlorination product of amyl chloride. The position of the two chlorine atoms (1 : 3) is demonstrated by the complete conversion of this compound into isoprene when its vapour is passed over soda lime.

β-methyltetramethylene dichloride,

$$CH_2Cl \cdot CH(CH_3) \cdot CH_2 \cdot CH_2Cl, \text{ boiling at } 170° \text{ to } 172° \text{ C.},$$

likewise yields isoprene by the action of soda lime, and appears to be a new compound not hitherto described.

Its constitution has been established by the following reactions:—

With potassium acetate, it gives a diacetate and a glycol—

$$CH_2Cl \cdot CH(CH_3) \cdot CH_2 \cdot CH_2 \cdot Cl \rightarrow \\ CH_3 \cdot COOCH_2 \cdot CH(CH_3) \cdot CH_2 \cdot CH_2OOC \cdot CH_3.$$

When heated with phosphorus tribromide this glycol yields a dibromide, which is converted into a dinitrile by the action of potassium cyanide. Saponification of the dinitrile yields β-methyladipic acid—

$$Br \cdot CH_2 \cdot CH(CH_3) \cdot CH_2 \cdot CH_2 \cdot Br \rightarrow CN \cdot CH_2 \cdot CH(CH_3) \cdot CH_2 \cdot CH_2 \cdot CN \\ \rightarrow HOOC \cdot CH_2 \cdot CH(CH_3) \cdot CH_2 \cdot COOH$$

All three dichlorides yield isoprene, together with small quantities of other unsaturated hydrocarbons, when the elements of hydrogen chloride are removed by passing their vapour over heated soda lime. Hence there is no advantage, from an industrial point of view, in proceeding to fractionate them, but the whole of the product boiling between 140° and 180° C. may be used.

The removal of the elements of hydrogen chloride is effected by passing the vapour of the dichlorides through a tube filled with fragments of soda lime and heated in an air bath at 470° C.; the products leaving the tube are condensed in a worm surrounded by a freezing mixture, and received in a condenser. The liquid is then fractionated into crude isoprene, boiling at 28° to 36° C., and into higher fractions still containing chlorine. Harries' apparatus may also be used for dechlorinating, heated only to 470° C.

The yield obtained, according to Perkin,[1] is about 40 per cent. of the theoretical.

The English process for the preparation of isoprene from isoamyl alcohol does not bear the impress, as we have been able to see, of great novelty. It is a return to the general methods, described long ago, for the formation of hemiterpenes, and, in particular, to the processes described by Reboul, in which these compounds are derived from amylene and its alcohols.

The substitution of chlorine for bromine permits of the industrialisation of the process, if isoamyl alcohol be procurable in sufficient quantity.

That is one great difficulty. The production of fusel oil, from which isoamyl alcohol is obtained, is somewhat restricted, and, on account of the numerous directions in which it is employed, the product is in great demand in the varnish and explosives industries.

"As far as one can estimate," says Perkin,[2] "the world's production of fusel oil, under present conditions, is only 3,500 tons, and, since it has a large number of uses, its price is about 3,500 francs (£140) per ton."

Under such circumstances it is highly probable that the realisation of the English synthetic method starting with isoamyl alcohol would have been impossible at a remunerative price. To ensure its success it was necessary to find an abundant source of isoamyl alcohol, at a low price.

"With a view to finding a remedy for this defect," continues Perkin, "we consulted M. Fernbach, of the Institut Pasteur, in order to discover methods of fermentation which would give more abundant yields of fusel oil than those at present in use in distilleries.

"It is, in fact, possible to obtain a considerably greater quantity of this product, since Ehrlich has shown that the addition of certain nitrogenous substances, such as leucin or other amino-acids, to the fermenting mass, results in the production of a larger proportion of higher alcohols."[3]

Fernbach[4] succeeded in finding a solution to the problem, putting forward a fermentation process, which enables the production, from starch, of acetone and fusel oil.

The yield is considerable, and the product entirely free from ethyl alcohol.

Under such conditions Fernbach's process would render the English synthesis indisputably practicable, and would permit of the preparation of isoprene under good conditions, provided always that the fusel oil obtained in this particular fermentation is rich in isoamyl alcohol.

"The fusel oil prepared by the Fernbach process," says Perkin, "has not the usual composition, but contains a large proportion of normal butyl alcohol."

But experiments have shown that under conditions similar to those which we have already described, butyl alcohol is converted into a lower homologue of isoprene, and yields only butadiene.

The butyl alcohol, obtained by the Fernbach process, would cost about £40 to £45 per ton, maize starch being valued at £10 per ton.

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[1] *J. Soc. Chem. Ind.*, 1912, 31, 616.

[2] *J. Soc. Chem. Ind.*, 1912, 31, 619

[3] Carr, in 1907, had proposed to start with wheat in order to synthesise rubber. He proposed to employ pytalin.

[4] Fernbach and Strange, Fr. Pat. 448,364, January, 1913.

We shall examine Fernbach's process, the patents for which have not long been published, and shall describe the method of fermentation. But, contrary to what Perkin seems to think, a number of investigators had already attempted the synthesis of fusel oil, and some of them had arrived at extremely interesting results, considerably before Fernbach had commenced his study of the question. The latter seems, moreover, to have derived a good deal of inspiration from the work of some of these earlier investigators.

Upon this point the bibliography drawn up by Bliss is undoubtedly incomplete, and we shall endeavour to fill up the gaps.

Fusel oil is not a definite compound, but a mixture of a number of different alcohols, ethers, organic acids, and aldehydes, its actual composition varying, not only with the source from which it is derived, but also with the conditions under which it is produced.

Butyl and amyl alcohols are the predominating constituents. Butyl alcohol was found to be present by Wurst, propyl alcohol by Chancel, hexyl alcohol by Faget, caproic acid and its esters by Rowney.

Fehling[1] found in the fusel oil obtained from molasses caproic acid, its esters, and neutral compounds; Perrot found amyl, butyl, and ethyl alcohols in the portion distilling between 80° and 110° C., but no propyl alcohol; the portion distilling between 140° and 300° C. contains only compound ethers. Surinam[2] isolated from this complex mixture the ethyl esters of œnanthylic and palmitic acids. Marckwald, who has recently taken up the study of fusel oils, found on examination of a large number of samples,[3] that the proportion of inactive *iso*amyl alcohol present varies with the raw materials employed. In fusel oil from potatoes it may reach as high as 48 to 50 per cent. This proportion is not characteristic of the oil from potatoes, that obtained from grain containing approximately the same amount of isoamyl alcohol.

Russian fusel oil, derived from potatoes, has been examined by Budakoff and Alexandroff,[4] who found in it :—

Isopropyl alcohol, ...	8·7 per cent.
Isobutyl alcohol, ...	9·8 „
Fermentation amyl alcohol, . .	87·4 „
Hexyl alcohol, aldehydes, and furfurol, ...	traces.

The character of a fusel oil also depends to a great extent upon the nature of the ferments employed in its production, and it is upon this fact that Fernbach claims to have based his process for isolating the special bacterium, with the aid of which starch can be converted into acetone and fusel oil.

For example, the beer organism, *Mycoderma cerevisiae*, gives isobutyl and isoamyl alcohols, whilst the wine organism, *Mycoderma ellipsoidus*, gives normal amyl alcohol.

Wyschnegradsky concludes, from his experiments on fusel oil, that only the three amyl alcohols, the normal alcohol, isoamyl alcohol, and methylethyl carbinol are present in abundance, only traces of the various other compounds being present.

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[1] *J. de Pharmacie*, 1854, 25, 74.

[2] *Jahresbuch*, 1858, 302.

[3] *Ber.*, 1902, 35, 1595; 1904, 37, 1038.

[4] *Chem. Zeit.*, 1903, 28, 187.

Rabuteau[1] determined the composition of fusel oil from potatoes by the analysis of one litre, and obtained the following figures :—

Isopropyl alcohol,	150	parts.
Propyl alcohol,	30	,,
Isobutyl alcohol,	50	,,
Normal butyl alcohol,	65	,,
Methylpropyl carbinol,	60	,,
Isoamyl alcohol,	275	,,
Water,	125	,,
Ethyl alcohol, aldehyde, ethyl acetate,	75	,,
Products boiling at 132° C., and containing amyl alcohol,	170	,,

Morin[2] finds that the fusel oil which can be separated from new Charentes cognac contains :—

Ethyl alcohol,	130	parts.
Normal propyl alcohol,	25	,,
Isobutyl alcohol,	25	,,
Amyl alcohol,	175	,,
Furfurol,	2	,,
Wine oils,	7	,,
Water,	7	,,

On the other hand, the following are comparative analyses, by the same author, of fusel oil from 100 litres of cognac and from the products resulting from the fermentation of 100 kilos. of sugar :—

	Cognac.	Sugar.
Aldehyde,	traces	traces
Ethyl alcohol,	50·837 grms.	50·615 grms.
Normal propyl alcohol,	27·17 ,,	2 ,,
Isobutyl alcohol,	6·52 ,,	1·5 ,,
Amyl alcohol,	190·21 ,,	51 ,,
Furfurol bases,	2·19 ,,	..

Kiliani[3] finds that fusel oil obtained from grain or potatoes contains more particularly methylethylcarbinol, whereas that obtained from molasses contains from 50 to 75 per cent. of isopropylcarbinol.

Karl Windisch gives the following as the composition of one kilo. of fusel oil obtained from potatoes, after it has been freed from ethyl alcohol and water :—

Normal butyl alcohol,	68·54	grms.
Isobutyl alcohol,	243·50	,,
Amyl alcohol,	678·60	,,
Free organic acids,	0·11	,,
Organic esters,	0·20	,,
Furfurol and bases,	0·05	,,

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[1] *Comptes rendus*, 1878, 87, 501.

[2] *Comptes rendus*, 1887, 105, 1019.

[3] *Monatsh.*, 1903, 24, 533.

The free acids and esters have the following composition :—

Capric acid,	36 per cent.
Pelargonic acid,	12 ,,
Caprylic acid,	32 ,,
Caproic acid,	14 ,,
Butyric acid,	0·5 ,,
Acetic acid,	3·5 ,,

Fusel oil from grain gives the following result on analysis :—

Normal propyl alcohol,	36·9 grms. per kilo.
Isobutyl alcohol,	157 ,,
Amyl alcohol,	758·5 ,,
Hexyl alcohol,	1·3 ,,
Free acids,	1·6 ,,
Esters,	3·05 ,,
Terpenes,	0·33 ,,
Terpin hydrate,	0·48 ,,
Furfurol, heptyl alcohol, bases,	6·21 ,,

The free acids and the esters have the following composition :—

	Acids.	Esters.
Capric acid,	44·1 per cent.	40·7 per cent.
Caprylic acid,	26·7 ,,	34·8 ,,
Caproic acid,	13·2 ,,	9·6 ,,
Butyric acid,	0·4 ,,	0·4 ,,
Pelargonic acid,	12·9 ,,	14·2 ,,
Acetic acid,	2·7 ,,	0·3 ,,

Rayman and Kries' analyses indicated the presence of a still larger proportion of amyl alcohol in potato fusel oil. Their results were as follows :—

Ethyl alcohol,	48·88 grms.
Normal propyl alcohol,	0·85 ,,
Isobutyl alcohol,	4·19 ,,
Amyl alcohol,	942·42 ,,
Hexyl alcohol,	0·19 ,,
Ethyl caprate,	0·26 ,,
Amyl caprate,	1·0 ,,
Capric acid,	0·66 ,,
Other constituents,	1·45 ,,

Le Bel states that fusel oil obtained from white wine is the richest in higher alcohols, whilst that obtained from sugar is the least rich.

Long and Linebarger examined American fusel oil obtained by the fermentation of wheat or other grain, and found that on fractional distillation it yielded the following fractions (per litre) :—

80° to 90° C.,	17 c.c.
90° to 95° C.,	8 ,,
95° to 105° C.,	30 ,,
105° to 115° C.,	55 ,,
115° to 120° C.,	95 ,,
120° to 125° C.,	240 ,,
125° to 130° C.,	515 ,,
130° to 135° C.,	25 ,,

Optically active and inactive amyl alcohols constitute the major portion of this product ; isobutyl and isopropyl alcohols are present in feeble traces only. These results have been confirmed by Hustinger,[1] Bamberger and Einhorn,[2] and Bechmann,[3] who, however, also discovered the presence of small quantities of pyridine, 2-5-dimethylpyridine, and their homologues. To sum up, as stated in Thorpe's *Dictionary of Chemistry*,[4] fusel oil, whatever its origin and method of preparation, is a very complex mixture, in which amyl and butyl alcohols predominate, and in which the following alcohols are also present :—

Ethyl, normal propyl, isopropyl, normal butyl, isobutyl, tertiary butyl, optically active amyl, optically inactive amyl, primary amyl, methylpropyl carbinol, isoamyl, primary hexyl, and primary heptyl, together with pyridine, aldehydes, and furfurol, various esters of capric, caprylic, caproic, acetic, formic, butyric, and pelargonic acids, free organic acids, terpenes, and terpin hydrate.

Of these bodies, isoamyl and butyl alcohols seem to be of especial interest from the point of view of caoutchouc synthesis ; for if we refer to Perkin's description of the English processes, we shall see that it is these which constitute the raw material, from which it is possible to obtain either butadiene or isoprene, of the various derivatives of divinyl, which on polymerisation yield a rubber. It will be of interest to summarise the properties of these alcohols.

Normal butyl alcohol is found in fusel oil in admixture with a good number of impurities ; by the use of the more modern methods, involving the action of pure cultures on the raw material, a much purer product is obtained. Emmerling states that this alcohol is found in especially large quantity in fusel oil from potatoes, whereas only traces of it occur in the product from grain.

To estimate its quantity he fractionates the fusel oil with a fractionating-column, converts the alcohol into iodide and then into acetate, which on hydrolysis yields the alcohol, boiling at 116° C. It can be obtained in much greater quantity by the fermentation of glycerin with *Schizomycetes ;* 6 to 7 per cent. can be obtained in this way.

The purified alcohol has a high refractive power ; when inhaled its vapour produces coughing, and it has a very unpleasant smell.

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[1] *Chem. Zeit.*, 1882, 6, 965.

[2] *Ber.*, 1897, 30, 224.

[3] *Journ. of Distillery*, 1912, 19, 300.

[4] Vol. II., p. 169.

Its density is 0·8239 at 0° C.; it dissolves in 12 parts of water at ordinary temperature, and separates from its solution on the addition of calcium or sodium chloride.[1]

Isobutyl alcohol is the second of the four possible isomerides of butyl alcohol; it is extracted from fusel oils, in which it occurs in variable amount, according to the raw material used and its method of formation. It is found, more particularly, in the oil obtained from potatoes, and is generally known under the name of fermentation butyl alcohol.

Wurtz, by whom it was first isolated, obtained it in large quantity from the alcohol prepared from beetroot. The best method of preparation is undoubtedly by the treatment of sugar molasses by fractional distillation, collecting only those portions which pass over between 85° and 125° C.

The first fractions are washed and rectified, the portion distilling above 104° C. being collected and boiled with caustic potash under a reflux condenser for four hours, then dehydrated with lime and finally rectified.

A pure alcohol is thus obtained. It is a colourless liquid more mobile than amyl alcohol, and having a slightly vinous odour; some observers state that it has an odour resembling that of syringa.

It is soluble in 12 parts of water at 18° C., and can be separated from its solution by the addition of calcium chloride, or of alkaline carbonates or phosphates.

It yields a crystalline compound with calcium chloride, and a syrupy product with zinc chloride.

It boils at 108° C., and its density is 0·8106 at 0° C. It serves for the preparation of synthetic musk by Baur's method—viz., by the nitration of a mixture of the alcohol with toluene and xylene.

Amyl Alcohols.—Eight isomerides, of the empirical formula $C_5H_{11} \cdot OH$ are known, viz.:—

		Boiling Point.
Normal amyl alcohol,	$CH_3 \cdot [CH_2]_3 \cdot CH_2 \cdot OH$,	137·0° C.
Isobutyl carbinol,	$(CH_3)_2CH \cdot CH_2 \cdot CH_2 \cdot OH$,	131·4
Active amyl alcohol.	$C_2H_5 \cdot CH(CH_3) \cdot CH_2 \cdot OH$,	128·7
Tertiary butyl carbinol,	$(CH_3)_3C \cdot CH_2 \cdot OH$,	102·0
Methylpropyl carbinol,	$C_3H_7 \cdot CH(CH_3) \cdot OH$,	118·5
Diethyl carbinol,	$(C_2H_5)_2CH \cdot OH$,	116·0
Methylisopropyl carbinol,	$(CH_3)_2CH \cdot CH(CH_3) \cdot OH$,	112·5
Dimethylethyl carbinol,	$C_2H_5 \cdot C(CH_3)_2 \cdot OH$,	102·5

Of these alcohols, it will be noticed that four are primary, three secondary, and one tertiary. Also, that three of them contain an asymmetric carbon atom, and are, therefore, capable of existing in three forms, the inactive, the dextro-rotatory, and the lævo-rotatory. There are thus altogether fourteen isomeric and stereoisomeric amyl alcohols.

Active amyl alcohol (methylethyl carbin carbinol) has a density of 0·8150 at 15° C.

Isobutyl carbinol—$(CH_3)_2CH \cdot CH_2 \cdot CH_2 \cdot OH$—occurs, mixed with a little active amyl alcohol in the amyl alcohol of fermentation.

It is found also in the tigelic and angelic esters of Roman camomile oil.

It is often produced by the fractional distillation of potato fusel oil,

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[1] Le Bel and Green, *Annales de Chimie*, 1880, 2, 24.

or from butyl alcohol which is converted into valeric acid by Balbiano's method.

Freundler and Damond prepare it in large quantity[1] from acetone oils. They first extract the methylethyl ketone, and on reducing this by the method of Sabatier and Senderens they obtain secondary butyl alcohol, which they then convert into bromide by means of phosphorus tribromide.

The organo-magnesium compound, prepared by Grignard's reaction, is then treated with the theoretical quantity of trioxymethylene, a yield of about 73 per cent. of amyl alcohol, and 7 per cent. of aldehyde—$C_5H_{11} \cdot CHO$. Although this process is very ingenious, it could not be used industrially on account of the high cost of the products employed.

Pure amyl alcohol is a colourless liquid, with a neutral reaction, which is unaffected even by exposure to light. It has a peculiar odour, productive of headache, and a burnt flavour; it is this which gives its burnt or empyreumatic taste to *raw* spirit. It leaves an oily stain on paper, which disappears but slowly.

One part dissolves in 39 parts of water at 15° C., giving a solution with a density of 0·998; one part of water dissolves in 11·5 parts of amyl alcohol, and the limpid solution has a density of 0·835 at 15° C.

Amyl alcohol forms crystalline compounds with the chlorides of calcium (Handl), tin, and antimony (Bauer and Klein).

It is miscible in all proportions with alcohol, ether, chloroform, benzene, carbon disulphide, and carbon tetrachloride. It is also soluble in all proportions in glacial acetic acid diluted with an equal volume of water, and can in this way be differentiated from the neutral amyl esters, such as formate, acetate, butyrate, pelargonate, valerate, etc., which are not soluble in this mixture.

From the analytical point of view, the presence of amyl alcohol may be detected by the following reactions:—

When heated with twice its own volume of sulphuric acid, it yields amylsulphuric acid, with a brown colouration and a leathery smell. In presence of sugar or other carbonisable organic matter this test fails, and it then becomes necessary to separate the alcohol by fractional distillation.

When heated with formic and sulphuric acids an odour of peaches is produced, resulting from the formation of amyl formate. Similar reactions occur with acetic and valeric acids, the odour characteristic of amyl acetate or valerate respectively being produced.

The quantitative determination of amyl alcohol may be carried out by carefully oxidising it with chromic acid and estimating the valeric acid formed.

Diethyl carbinol can be obtained by diluting with water the product of the reaction between zinc ethyl and ethyl formate.[2] It has a density of 0·832, and on oxidation yields diethyl ketone.

Methyl-*n*-propyl carbinol can be obtained from the corresponding iodide, or, according to Belohonbeck,[3] by reducing methylpropyl ketone with sodium amalgam. As thus prepared it is optically inactive and dissolves in 20 parts of water. It gives the iodoform reaction, and is converted by oxidation into methylpropyl ketone.

Methyl*iso*propyl carbinol is obtained from methyl*iso*propyl ketone by

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[1] *Comptes rendus*, 1905, 141, 830.

[2] Wagner and Saytzeff, *Annales de Chimie*, 1875, 175, 351.

[3] *Ber.*, 1876, 9, 924.

reduction with sodium amalgam (Runch[1]), or by adding water to the product of the reaction between zinc methyl and bromacetyl bromide, or chloracetyl chloride.[2] Its density at 0° C. is 0·833.

Tertiary amyl alcohol, or dimethylethyl carbinol, has a boiling point of 102° C., according to Perkin, and a density of 0·8144 at 15° C.

It may be prepared from tertiary amyl iodide, or by the action of zinc methyl on propionyl chloride.[3] It is a powerful narcotic.

Hexyl and caproyl alcohols, which boil at 150° C., are prepared by the fermentation of raisin skins. Secondary isoamyl alcohol may be prepared synthetically by the action of bromacetyl bromide or chloracetyl chloride on isobutylene oxide (Winogradoff,[4] Bogomoletz [5]).

Perkin, in his various communications on synthetic rubber, has described, as an absolutely new fact, the discovery by Fernbach of a ferment by means of which starchy material can be converted into fusel oil and acetone, with industrial yields.

However interesting Fernbach's processes, as described by Perkin, may be, it should not be supposed that the problem of the synthetic production of fusel oil has been attacked only by the chemist of the Institut Pasteur. Other chemists were dealing with the subject previously, and the industrial results which they obtained are able to stand comparison with those quoted by Perkin.

They have gone almost unnoticed because, in Europe, the interest in fusel oil has been relatively small, but they have been studied, and in many instances put on a commercial basis in America, where the use of fusel oil in the preparation of varnishes with a nitrocellulose basis has undergone enormous extension during the last twenty years.

We give below a *résumé* of the work published on this subject, and quote freely from Worden's excellent book, in which the subject of fusel oil has been dealt with very thoroughly.

Twenty years ago fusel oil, and the amyl alcohols, were regarded as troublesome by-products which were to be got rid of at any price; at the present time the production of amyl acetate and its use in the manufacture of varnishes have caused these products to be sought after, and their value has increased four-fold. Under these circumstances, since the natural sources of fusel oil, a by-product of the manufacture of ethyl alcohol are of necessity limited in extent, attempts have been made to produce it synthetically. Morin, in 1888,[6] found that normal amyl alcohol is produced in the fermentation of glycerin to the extent of 10 per cent. on the raw material taken. This fermentation is brought about by a special bacterium isolated by Fitz, *Bacillus butylicus*, the study and selection of which was afterwards taken up by Fernbach. Perdrix [7] found this bacillus in the Paris drinking water, and he found that it gave a yield of 105 to 110 c.c. of amyl and butyl alcohols per kilo. of potatoes.

"This bacterium," he says, "only develops in the absence of air, and grows much better in an atmosphere of hydrogen or carbon dioxide. Its optimum temperature is 35° C. and its maximum 43° C. Under favourable circumstances spores form completely in ten days; they differ from the *vibrio butylicus* of Pasteur and the *amylobacters* of Van Tieghem."

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[1] *Annalen*, 1876, 180, 339.

[2] Bogomoletz, *Annalen*, 1881, 209, 86.

[3] Popoff, *Annalen*, 1868, 145, 292.

[4] *Annalen*, 1878, 191, 125.

[5] *Ibid.*, 1881, 206, 70.

[6] *Comptes rendus*, 1888, 105, 819.

[7] *Zeit. f. Spirit. Ind.*

In 1896, Rayman and Kries, in a series of researches on the by-products of alcoholic fermentation, established the fact that amyl alcohol was produced by pure cultures derived from the beer yeast, but they did not determine the conditions necessary for its production. Later, they stated that they were certain that the formation of amyl alcohol by pure yeasts was not attributable to physiological conditions unfavourable to the development of the cells.

They found that pure distillery yeasts did not produce amyl alcohol in an artificial medium of glucose; but they found, on the other hand, that if barley wort were used, amyl alcohol appeared. They concluded that this alcohol is not produced by the fermentation of the hexoses (starch or sugar), but of the carbohydrates which accompany them, belonging to the class of substances known as *furfuroids*, which have been prepared by Tollens by the acid hydrolysis of the grain employed in brewing.

By sowing solutions of glucose containing peptone and nutritive salts, with pure cultures of *Saccharomyces cerevisiæ*, and allowing fermentation to proceed for several weeks, it was found that, in addition to ethyl alcohol, ammonia, sulphides, and organic bases were produced, but never amyl alcohol. In another series of experiments, in which grain used in the preparation of alcohol was allowed to ferment in presence of malt for eleven months, large quantities of amyl alcohol were obtained in addition to ethyl alcohol, aldehydes, and *furfuroids*.

Emmerling's experiments,[1] carried out with different kinds of ferments upon various carbohydrates, showed that under the normal conditions of alcoholic fermentation only minute quantities of fusel oil were formed so long as the yeasts remained pure.

On the other hand, this author observed that a good number of bacteria, and in particular *Granilobacter butylicum* and *Bacillus orthobutyricus* possessed the power of converting carbohydrates into higher alcohols, especially butyl alcohol. This is what Fernbach's bacterium does.

We must also mention, in this connection, the *amylic ferment* isolated by Pereire and Grignard.[2] This process has been patented.[3] It consists in fermenting a sugar solution by means of a culture of "*Vibrion amylique*," at 40° C., in presence of an excess of lime. When fermentation is sufficiently far advanced the liquor is cooled down to 24° C. and transferred to another vessel, in which it is mixed with distillery ferments, fermentation being then continued in the ordinary way. On distillation a spirit containing a high proportion of amyl and other higher alcohols is obtained.

Pereire and Grignard's ferment seems to be particularly active when it acts upon potato peelings, and it appears to be most advantageous to employ, as carbohydrates, hydrolysed potato starch and cane sugar. Thus, a kilo. of boiled potatoes and 50 grms. of ground wheat are left in contact with 3 litres of water and a little lime to which potato peelings are added; a yield of 25 c.c. of fusel oil is obtained. Under the same conditions 500 grms. of molasses, containing 48 per cent. of sugar, yield 19 c.c. of fusel oil. The same materials, saccharified by malt, yield only 1·5 c.c. of fusel oil.

Emmerling found that the addition of decomposed ferment does not favour the formation of fusel oil.

In 1905,[4] continuing his researches on the fermentation of molasses by the

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[1] *Ber.*, 1904, 37, 353.

[2] *J. de la Soc. pour l'Ind. chim.*, 1902, 21.

[3] Eng. Pat. 316,062 of 1901.

[4] *Ber.*, 1905, 38, 953.

bacteria present on potato skins, he found that it was necessary to dilute to a 10 per cent. sugar content, because with higher concentrations lactic acid was formed. The yield of total alcohol was 4·8 per cent. on the molasses or 8·9 per cent. on the sugar. The fermentation product was found on separation to contain much ethyl and *n*-propyl alcohol, but chiefly *n*-butyl alcohol, amyl alcohol being almost entirely absent.

It would seem, from Perkin's memoir, that Fernbach obtained almost identical results. The bacterium appears to be an anærobe, yielding better results in the absence of air. The activity of fresh cultures diminishes as they age; further, it is found that if alkali, such as lime, be absent, the production of higher alcohols falls off, and the greater part of the sugar is converted into acids of the fatty series, chiefly butyric acid, oxidation taking place.

Pringsheim has confirmed Emmerling's observations, with regard to the existence of a bacterium which converts potatoes into fusel oil, but he was not able to obtain satisfactory and well-controlled yields.[1] Pringsheim digested American potatoes, cut up into pieces, for several days with water. He thus isolated three kinds of organism from the slime—viz., a *cœcus*. a bacterium identical with *Bacillus mesentericus vulgaris*, and the "*fusel oil bacillus*."

The last-named is a motile rod-shaped organism, which converts potatoes into viscous material, much hydrogen and carbon dioxide being liberated during the process, and amyl alcohol formed. After the spores are formed, the rods swell up into the form of elongated cells. They survive for sixty minutes at a temperature of 80° C. It has been observed that they do not develop on potatoes in presence of 10 per cent. alcohol; it follows that it is not very likely that this bacillus is the cause of the production of fusel oil in the distillery vats. It has also been noticed [2] that the rate of formation of fusel oil is retarded by the presence of certain inorganic salts, notably ammonium sulphate, in proportion to their amount. Thus, on fermenting 175 lbs. of rice, 75 lbs. of maize, and 80 lbs. of malt in 2,000 litres of water, 5 litres of fusel oil were obtained. On adding 250 grms. of ammonium sulphate only 2½ litres were obtained; with 500 grms. 2 litres, and with 1 kilo. none.

Ehrlich has put forward an explanation of this phenomenon, to which we shall refer again later. Buchner and Neresheimer [3] found that in fermentation by yeast juice—obtained by compression—only traces of fusel oil were formed. Buchner dwelt very fully upon this reaction in a lecture before the Chemical Society of Paris.

Windisch [4] followed up the work of Rayman and Kries by investigating the action of old, rejuvenated, and fresh yeasts on sugar solutions. He found that the age of the ferment in no way influenced the formation of the amyl alcohols. Moreover, he found that the organisms which facilitate the formation of amyl alcohols develop best in presence of certain carbohydrates. Thus, in an artificial nutritive solution, sown with pure distillery yeast, to which a trace of fusel oil was added, amyl alcohol always appeared. He concluded that the source of the latter is not in the hexoses, but in the other fermentable sugars, formed by hydrolysis of the polysaccharides present in the raw materials. Lindet [5] also studied this question. He prepared

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[1] *Ber.*, 1905, 38, 953.

[2] *Biochem. Zeit.*, 10, 490.

[3] *Ber.*, 1906, 39, 3201.

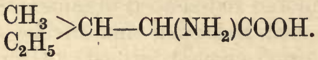
[4] *Zeit. f. Spirit. Ind.*, 1904, 27, 34.

[5] *Comptes rendus*, 1891, 112, 663.

two solutions, one of cane sugar, the other of glucose, and fermented them, successively, with a large and a small quantity of yeast. The solution with the large amount of yeast was found to contain 1·5 grms. of higher alcohols per litre, that with the small amount 2·5 grms., and the higher the temperature of fermentation the larger became the amount of fusel oil produced. Lindet concluded that the fusel oil is formed, not by the yeast, but by other organisms present with it as impurities. Ehrlich's experiments[1] have thrown an interesting light upon the obscurity of the formation of fusel oil.

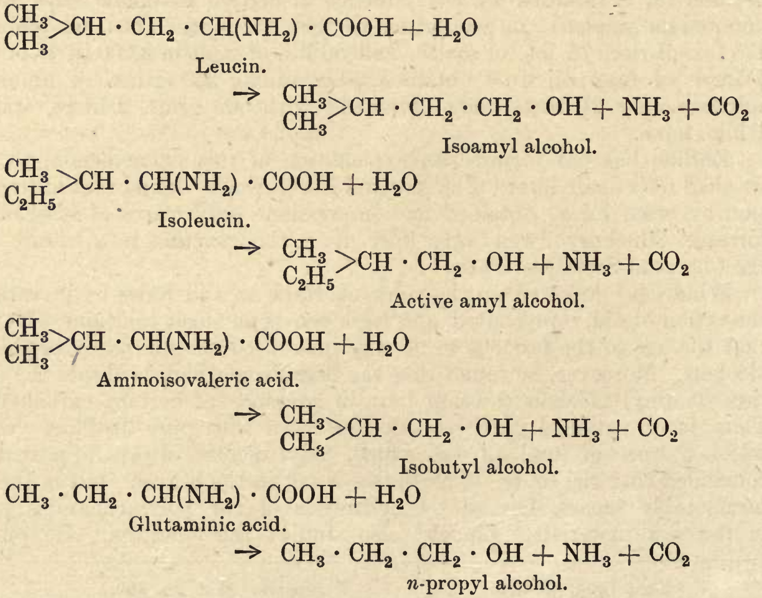
Adopting a theory propounded by Müller in 1857, which assumed that fusel oil is formed as a result of the action of ferments upon the proteins present in the raw material, he maintained that sugar plays no part at all in their formation. He showed that fusel oil resulted from the decomposition of protein material—such as the amino-acids—by bacterial action, or by the auto-fermentation of yeast. At the conclusion of an extensive series of experiments, he showed that *isoleucin*, which can be separated from the uncrystallisable portion of the residue obtained on treating molasses with strontia, is the normal source of fusel oil.

Isoleucin, which is the first of the known amino-acids, contains two asymmetric carbon atoms—



$$\begin{matrix}CH_3\\C_2H_5\end{matrix}\!>CH—CH(NH_2)COOH.$$

It is a methylethylaminopropionic acid, which is closely related to optically active amyl alcohol. The latter can be obtained from *isoleucin* through the aldehyde and hydrogen cyanide, with subsequent hydrolysis. Similar relations exist between *leucin* and isoamyl alcohol, and between isobutyl and *n*-propyl alcohols and the corresponding amino-acids :—



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!>CH \cdot CH_2 \cdot CH(NH_2) \cdot COOH + H_2O$$

Leucin.

$$\rightarrow \begin{matrix}CH_3\\CH_3\end{matrix}\!>CH \cdot CH_2 \cdot CH_2 \cdot OH + NH_3 + CO_2$$

Isoamyl alcohol.

$$\begin{matrix}CH_3\\C_2H_5\end{matrix}\!>CH \cdot CH(NH_2) \cdot COOH + H_2O$$

Isoleucin.

$$\rightarrow \begin{matrix}CH_3\\C_2H_5\end{matrix}\!>CH \cdot CH_2 \cdot OH + NH_3 + CO_2$$

Active amyl alcohol.

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!>CH \cdot CH(NH_2) \cdot COOH + H_2O$$

Aminoisovaleric acid.

$$\rightarrow \begin{matrix}CH_3\\CH_3\end{matrix}\!>CH \cdot CH_2 \cdot OH + NH_3 + CO_2$$

Isobutyl alcohol.

$$CH_3 \cdot CH_2 \cdot CH(NH_2) \cdot COOH + H_2O$$

Glutaminic acid.

$$\rightarrow CH_3 \cdot CH_2 \cdot CH_2 \cdot OH + NH_3 + CO_2$$

n-propyl alcohol.

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[1] Ger. Pat. 177,174 of 1905.

These reactions indicate that isobutyl alcohol is formed from butylalanine, or amino*iso*valeric acid, and *n*-propyl alcohol from glutaminic acid during fermentation. The amyl alcohol thus formed remains in the solution as fusel oil, whilst the ammonia is absorbed by the yeast and re-converted into protein.

The experimental proof of these facts is furnished by the following observation :—When pure yeast acts upon sugar no formation of ammonia can be observed at any moment; on the other hand, if yeast killed by acetone, and, therefore, containing no enzymes capable of protein synthesis, be taken, it is unable to convert leucin into fusel oil. Ehrlich fermented a large number of solutions containing 5 to 10 per cent. of sugar, and continued the process until the whole of the sugar was converted; he found that the solutions containing leucin fermented more rapidly than the others. By the addition of this compound the percentage of fusel oil in the alcohol can be increased from 0·4 to 3 per cent., and the quantity is strictly proportional to the amount of leucin consumed.

The addition of asparagin or of ammonium carbonate diminishes the percentage of amyl alcohol formed. By means of a special enzyme, endotryptase, proteins are decomposed not into peptones but into amino-acids.

The mechanism of the formation of amyl alcohol is, therefore, intimately bound up with the formation of proteins in yeast, and is inseparable from it. Ehrlich draws the conclusion also that the formation of the other higher alcohols and of a portion of the fatty acids has its origin in the other members of the amino-acid series present. It is known, moreover, that Effront has succeeded, with the aid of *amydase*, in extracting from the vinasse residuals rich in amino-acids, the whole series of fatty acids from formic to butyric.

Not only is it possible to extract these compounds from valueless residuals, as is done on a factory scale at the Nesles distillery, but from these same residuals it is possible, without recourse to Fernbach's process in which starch is employed, to extract all the alcohols—isoamyl or butyl—necessary for the synthesis of rubber. The cost of production by this method must certainly be very low.

We have the following ascertained facts, therefore :—

With pure yeast and pure sugar—no fusel oil produced.

With the same mixture and leucin—inactive amyl alcohol produced.

With the same mixture and isoleucin—*d*-amyl alcohol produced.

When a mixture of *d*- and *l*-leucin is employed only the lævorotatory amino-acid is attacked.

The yeast poorest in nitrogen produces most amyl alcohol.

In ordinary fermentation fusel oil is formed from the leucin, isoleucin, valine, and tyrosin resulting from the auto-hydrolysis of the yeast; when yeast killed with acetone is used no fusel oil is formed.

From these facts it follows that the whole series of higher alcohols can be obtained by fermentation from the various amino-acids contained in the distillery residues, and the latter, therefore, become a valuable raw material in view of the synthesis of rubber.

The limit to the formation of fusel oil is the reconstitution of proteins by yeast; thus it can only be produced in abundance in the presence of excess of acid. It is probable that the phenomenon of conversion takes place in the following manner :—Under the influence of the enzymes the amino-acids give off ammonia and combine with water; the new compound is then decomposed into carbon dioxide and alcohol, in the same way as lactic acid is decomposed into carbon dioxide and ethyl alcohol. The formation of optically active alcohols can only take place in the presence of amino-acids containing an asymmetric carbon atom, such as isoleucin.

Ehrlich has attempted to isolate from yeast the particular enzyme which is responsible for the conversion of the amino-acids into fusel oil, but so far his efforts have not been successful.

The fermentation of the amino-acids appears to be a general biological phenomenon, accompanying the synthetic formation of the albumins; it results in a degradation of the molecule and not a condensation, as in Fischer's syntheses of the polypeptides.

Effront, whose very extensive work on the subject we have quoted, has explained how the decomposition of the amino-acids, during ordinary fermentation, is brought about, and has shown that it is possible to break them down into fatty acids and ammonia by the action of a particular enzyme, *amydase*. In an alkaline medium, and especially in presence of alumina, at 40° C., *amydase* completely decomposes the amino-acids in 70 hours; this enzyme can be isolated.

The theory of the formation of fusel oil which we have just set forth is in agreement with the researches of Fischer and his pupils, Mendel and Levine, on the polypeptides; but it differs from the theory of the formation of amino-acids in putrefaction. This question has been investigated by Abderhalden, Hirsch, and Schuler,[1] as regards isoleucin by Abderhalden and Brossa,[2] as regards phenylalanine by Ley and Ulrich,[3] by Weichardt, Takeuclin and Inouë.[4]

In the synthesis of fusel oil, based on the principles which we have just explained, it is necessary to have at disposal, in large quantity and at low price, either leucin or similar products. Leucin is obtainable from all sorts of waste material rich in albuminoid nitrogen. This part of the problem offers relatively few difficulties.

A very important source of leucin will certainly be found in the residual liquors from the treatment of sugars with lime and strontia. Leucin can be isolated from them by crystallisation in a high state of purity, and these residues are at present put to no important use. The uncrystallisable residues of beet sugar refineries are also an abundant source of diamino-acids, and the same is true of the residual liquors of starch manufacture, of horn débris, and lastly of slaughter-house blood.

Ehrlich has patented the preparation of fusel oil[5] from peptonised or hydrolysed albumins, or from mixed amino-acids, treated with distillery ferments in presence of worts or molasses. The fusel oil produced is separated from the ethyl alcohol in the usual way.

Fresh progress has been realised, in this method of synthetic preparation of fusel oil, by Pringsheim,[6] who found, in a fusel oil prepared from maize, isopropyl and normal butyl alcohols, in addition to the isobutyl, *n*-propyl, and amyl alcohols ordinarily found in this mixture. These alcohols are the products of fermentation by the butyric bacillus, and Pringsheim concluded from this that the fusel oil in question was produced by two distinct processes:—(1) The breakdown of the amino-acids in accordance with Ehrlich's views;

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[1] *Ber.*, 1909, 42, 3394.

[2] *Ibid.*, 1909, 42, 3411.

[3] *Ibid.*, 1909, 42, 3440.

[4] Tokio, 1899.

[5] Eng. Pat. 6,640 of 1906; Ger. Pat. 177,174 of 1905.

[6] *Biochem. Zeit.*, 1909, 16, 243.

(2) butyric fermentation. In support of these views he drew attention to Rabuteau's analyses of fusel oil, which show that isopropyl and *n*-butyl alcohols are present in it; butyric fermentation would, therefore, provide a means for the synthesis of fusel oil. The proof of this dual mode of formation is to be found in the fact that if wort be fermented in presence of ammonium sulphate, fusel oil cannot be formed, because the amino-acids are not decomposed. In such fermentation isopropyl and *n*-butyl alcohol are, however, formed, and the conclusion to be drawn is, therefore, that their formation is due to the action of the butyric bacillus upon the sugar. This would also explain pretty clearly why Fernbach's bacterium, in acting upon starch, gives mainly butyric acid, and it is probable that this bacterium is only a variety of the butyric bacillus. Other investigators, prior to Fernbach, have endeavoured to effect the synthesis of fusel oil.

Sultan and Stern[1] patented the production of fusel oil, starting from albuminous material rich in nitrogen. They increased the yield by the addition of leucin, obtained by the decomposition of casein or fibrin. From 1,000 kilos. of potatoes, 20 kilos. of malt, and 25 kilos. of leucin, they obtained 120 litres of rectified spirit, and 10 kilos. of amyl alcohol; and from 1,000 kilos. of molasses containing 50 per cent. of sugar, they obtained 300 litres of ethyl alcohol and 40 kilos. of amyl alcohol.

Mislin and Lewin put forward a method[2] based on the following principles:—They propose to add to musts, fermented with malt, potatoes, maize, cereals, seeds of leguminosæ rich in nitrogen, or distillation residues. The organisms obtained in the fermentation of dried grapes and plums are then sown into it, and the whole is made alkaline before fermentation begins, by the addition of lime. Fermentation goes on for 120 to 150 hours, and after this the liquor is distilled. A mixture of fusel oil and acetone is obtained, somewhat as in Fernbach's process. René Locquin[3] prepared large quantities of synthetic isoamyl alcohol, starting with isobutyl chloride and applying Grignard's reaction. By condensing the magnesium isobutyl chloride with trioxymethylene, isoamyl alcohol is obtained.

It will be seen that the methods of synthesis of fusel oil at present known are pretty numerous, and some of them appear to be capable of yielding industrial results when they have been thoroughly investigated.

Those which are of very great interest are especially those which aim at making use of the vinasse residuals of the distillery, and by-products of sugar refineries and starch mills.

It is to be hoped that in France, a great productive centre of sugar and alcohol, and where the Effront process for preparing fatty acids from these residues has been an undisputed success, a thorough study of this question will be undertaken, so that the country may not be outdistanced by Germany or England in this connection. The production of ammonia, which accompanies the production of fusel oil, will, moreover, pay the greater part of the cost of preparing the higher alcohols by these methods, and will enable a raw material for the manufacture of synthetic rubber to be obtained at a low price.

Fernbach's process,[4] although it forms in a sense the keystone of the English synthesis—for, without it, this is economically unrealisable—was kept

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[1] Fr. Pat. 365,619 of 1906.

[2] Eng. Pat. 10,435 of 1905; Fr. Pat. 354,807 of 1905.

[3] *Bull. Soc. Chim.*, 1904, 31, 599.

[4] Fr. Pat. 448,364, Sept. 16, 1912.

secret up to January 29th, 1913, the date on which the patent—applied for in France on September 16th, 1912—was published.

We give below the specification *in extenso*, because the whole thing is of too great importance to be passed over with a brief analysis, or a simple summary :—

" The object of the present invention is the manufacture of acetone and of the higher alcohols from carbohydrates in a very economical and efficient way, and with a good yield, and so that if desired the process may be carried on continuously over a considerable period of time.

" According to this invention, carbohydrates, such as maize, potatoes, glucose, or substances extracted from woody material by treatment with superheated steam or with acids, or mixtures of these materials, are taken, and from them a wort is prepared with a large quantity of water ; this wort is then sterilised, a process which may be accomplished by heating at a temperature of 130° C. A small quantity of yeast, degraded, as described later, either by the action of a ferment such as *tyrothrix tenuis* in presence of sterilised air, or by means of steam, or water heated under pressure, is also added before or after sterilisation.

" The mixture may then be kept at a high temperature for a certain time, and, after cooling, a ferment of the type of the *bacillus butylicus* of Fitz is added to it, care being taken to prevent the access of air during the fermentation, and to maintain a temperature suitable for fermentation until the latter is completed.

" The mass is then distilled, and the distillate, which consists mainly of water, acetone, and higher alcohols, may be separated into its constituents by fractional distillation or other suitable means. The degraded yeast, referred to above, is prepared by taking yeast, as produced, for example, in the fermentation industries, mixing it with water, and sterilising it ; this may be accomplished by heating it, at a sufficiently high temperature, for a certain time.

" The mixture is cooled and a ferment of the type of *tyrothrix tenuis* is added to it ; sterilised air may then be allowed to have access to the mixture during the period of fermentation, or at certain intervals during this period. When fermentation is at an end it has been found that about 90 per cent. of the nitrogenous constituents of the yeast has been converted into a soluble form, which is not precipitated by tannin.

" Instead of degrading the yeast by means of the above-named ferment it may be degraded by means of steam or water under pressure.

" It has been found an advantage to conduct fermentation in a closed vessel, connected with an aspirator and to a condenser, the aspirator being worked so as to obtain a reduced pressure, and thus to remove from the fermentation vessel the whole or the greater part of the substances which are volatilised with water vapour at the temperature of fermentation.

" By this means the process can be made a continuous one, if the fermentation vessel be provided with means for introducing the sterilised water and the materials to be fermented, as well as the degraded yeast referred to above.

" The reduction of pressure effected by means of the aspirator may, for example, with an aqueous wort at a temperature of 30° to 40° C., amount to at least 150 mm. of mercury, absolute, in the absence of any considerable evolution of gas. If gas is given off to any considerable extent a high vacuum may not be necessary. If desired, any gaseous substance, as distinguished from condensable vapours, may be absorbed by alkali or other chemical agent capable of combining with the said gaseous substance, before the vapours reach the condenser. For example, carbon dioxide, CO_2, may be absorbed by passing the gases and vapours through a solution of caustic soda, or through milk of lime.

" Although the applicants have described above the simultaneous employment of the degraded yeast referred to above and of a reduced pressure, in carrying out the fermentation with a ferment of the type of the *bacillus butylicus* of Fitz in the absence of air, in certain cases either the degraded yeast or the pressure reduction may be eliminated from the process.

" By working under the conditions set forth above it is possible to convert 33 to 50 per cent. of the carbohydrate employed into a mixture of acetone and higher alcohols, in the proportion of about 2 parts of the latter to 1 of acetone. The following examples show how the invention may be carried out; nevertheless, it will be understood that the invention is not limited to these examples :—

" **Preparation of the Degraded Yeast suitable for Use in the Process.— Example No. 1.**—About 50 kilos. of pressed yeast is mixed with about 500 kilos. of water, and the mixture is sterilised by heat, a temperature of about 130° C. being employed, maintained for several hours.

" The mixture is then cooled, preferably to a temperature of 30° to 35° C., and a ferment of the type of *tyrothrix tenuis* is added, in presence of sterilised air, care being taken to see that no other ferment gains access to the mixture. The mixture is kept preferably at a temperature of 30° to 35° C. for four to five weeks, sterilised air being admitted at intervals of four hours, for example. Towards the end of four or five weeks about 90 per cent. of the nitrogen content of the mixture is converted into a form which is not precipitable by tannin.

" **Example No. 2.**—About 50 kilos. of pressed yeast and 500 kilos. of water are kept at a temperature of about 150° C. for twenty-four hours, or until a sufficiently large proportion of the nitrogenous matter of the yeast is converted into a form which is not precipitated by tannin. Acids or alkalies may be added to facilitate the conversion, but in this case all acid or alkali remaining free at the conclusion of the operation must be neutralised.

" The example which follows shows how fermentation is carried out, according to this invention, by the use of a ferment, such as the *bacillus butylicus* of Fitz, using at the same time the degraded yeast described above, together with reduced pressure, although, as has already been stated, the one may be employed without the other.

" **Example No. 3.**—About 15 kilos. of potato starch is mixed with 500 kilos. of water, in a closed vessel, connected with an aspirator and a condenser. To this mixture is added a quantity of the degraded yeast mentioned above, such as that which contains 250 grms. of soluble nitrogenous material, not precipitated by tannin.

" The mixture is then boiled for four hours at a pressure of about 9 kilos. The temperature is then reduced to 30° to 35° C., and a ferment of the type of the *bacillus butylicus* of Fitz is added, care being taken to exclude air during the fermentation. The aspirator is operated in such a way as to reduce the pressure in the fermentation vessel to a degree such that the acetone, the higher alcohols, and the water vapour are drawn off, and pass to the condenser.

" SUMMARY.

" The invention consists in a process of manufacture of acetone and higher alcohols from carbohydrates, having the following distinguishing features :—

" 1. The admixture of a carbohydrate with water ; the addition of degraded yeast ; the addition to the mixture, after sterilisation, of a ferment of the type of the *bacillus butylicus* of Fitz ; and the fermentation of the mass, air being excluded.

" 2. The aspiration of the vapours, or vapours and gases, as they are generated in the fermentation vessel, with or without absorption of gas before the vapours pass to the condenser.

" 3. The preparation, with a view to its employment in the specified process, of a food-material, by mixing yeast with water, sterilising the mixture, and subjecting it to the action of a ferment of the type of *tyrothrix tenuis*, in presence of sterilised air.

" 4. The preparation, with a view to its employment in the specified process, of a food-material, by degrading yeast by means of steam or of water heated under pressure, with the addition of an alkali or an acid.

" 5. The sterilisation of the carbohydrate material, after admixture with water."

Such is the discovery which Perkin has described as being " of the highest importance, not only from the special point of view of rubber, but also from that of other industries. If any doubt should remain on the subject it should be sufficient to remark that it has been investigated most minutely by Otto Hehner, who has fully confirmed Fernbach's results in every detail."

In spite of the authority of Otto Hehner, we cannot share Perkin's enthusiasm for Fernbach's discovery.

Excepting, perhaps, in so far as it relates to the production of acetone, it does not, in fact, teach us very much that we did not know before, and it appears to be only a corollary to the attempts already made to effect the synthesis of fusel oil—attempts which we have already described.

The inexact, often nebulous, manner in which the patent in which Fernbach's discovery is claimed is drawn up, does not exhibit the customary clearness of thought of the professor of the Institut Pasteur. Is it the necessity of working to instructions, and of having an inspiration on a fixed date, which has fettered him, and rendered his language so cloudy ? It is possible.

On referring to the document which we have just reproduced, and which we endeavoured to analyse, we find in it two different portions. One relates to the scientific principle underlying the conversion of starchy material into acetone and higher alcohols, by means of a special fermentation, and to the method of applying this principle ; the other relates to its industrialisation, and indicates the apparatus by means of which it may be worked as a continuous process.

The starchy material of whatever origin—for the patent tends to cover the preparation of fusel oil and of acetone from all fermentable substances, including even sawdust, from which, with such difficulty, Simonsen or Classens were able to obtain 5 grms. of alcohol per kilo.—the starchy material is subjected to the double action of a degraded yeast—this being, moreover, unnecessary—and of the *bacillus butylicus* of Fitz.

The use of this ferment was suggested long before Fernbach; it was he, however, who recognised that it did not give a fusel oil rich in amyl alcohol, but almost entirely butyl alcohol.

From this viewpoint, the aim pursued by Strange and Graham has not been achieved; for whereas from isoamyl alcohol, by means of the Perkin-Matthews' process, which has already been described, it is possible to prepare isoprene, and thus to synthesise normal rubber, from butyl alcohol it is only possible to obtain butadiene rubber, the properties of which from an industrial point of view are still an unknown quantity.

An explanation is hereby afforded of the comparatively cold reception which was given, by English technical journals, to the processes of Strange and Graham, when the Synthetic Products Company, Ltd., was floated.

In reality, and contrary to Perkin's statements, the synthesis of fusel oil was not achieved, but rather that of butyl alcohol. But if reference be made to the various analyses of fusel oil which have already been quoted, it will be found that amyl alcohol is the main constituent.

For example, the following is an analysis of fusel oil from potatoes by Windisch :—

ANALYSIS OF FUSEL OIL.

n-butyl alcohol,	68·54	grms.
Isobutyl alcohol,	243·50	,,
Amyl alcohol,	678·60	,,
Organic acids,	0·11	,,
,, esters,	0·20	,,
Furfurol and bases,	0·05	,,

Perkin himself admits, however, that butyl alcohol predominates, constituting the principal part of the fermentation products obtained by means of Fernbach's process.

From this fact it follows that the principal action must be due to Fitz's bacillus, and Fernbach and Strange's patent indicates this, moreover, when it states :—

"Although the applicants have described the simultaneous employment of degraded yeast and reduced pressure, in carrying out the fermentation with a ferment of the type of the *bacillus butylicus* of Fitz, in the absence of air, in certain cases either the degraded yeast or the pressure reduction may be eliminated."

This amounts to saying that the process is carried out only with Fitz's bacillus; but this reaction does not appear to be new, it seems to have been known for a long time.

The butylic ferment discovered by Fitz[1] is a bacillus, fairly large and fairly thick, with an average length of 5μ to 6μ and a width of 2μ.

"The young rodlet," says Duclaux, "is a little more slender than when it ages; it is also more thread-like and elongated in albuminous liquids, and stouter in liquids containing glycerin. It is non-motile when it is young, and develops in strongly aerated liquids; in a liquid free from oxygen, and during fermentation, its movements are rapid, and appear to be accom-

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[1] *Ber.*, 1878, 11, 13, 481, 878.

panied by rotation about an axis. It can live and develop in solutions of calcium lactate, ammonium lactate, glycerides, erythritol, malates, tartrates, citrates, and lactose, without fermenting them, whereas it ferments sugar, glycerin, and mannitol very vigorously.

"This is a singular fact, and may be explained in the following way:—The anærobic butylic ferment is only able to ferment those substances with sufficient energy to supply its particular vital requirements, and leaves the others, whilst still able to live in contact with them, and even to make use of the materials of which they are built up, provided there is always excess of oxygen at its disposal, and that it can find in that the excess of energy with which these non-fermentable materials are unable to provide it in the absence of air."

The maximum of activity, from the point of view of fermentation, of the bacillus of Fitz is in the absence of air, and this is, moreover, a condition which Fernbach and Strange have religiously observed.

Fitz's bacillus is only able to react with sugar in the form of glucose or of invert sugar, and it is unable to convert starch direct, since it does not secrete amylase. The starch must, therefore, be first saccharified before it can be acted upon by the bacillus. The latter can make use of various albuminoid materials as a source of nitrogenous nutriment, and it secretes one or more diastases capable of liquefying fibrin, casein, gluten, and albumin, a result which is obtained without liberation of gas. The temperature most favourable to its action lies between 35° and 40° C., and from 42° C. upwards marked diminution occurs until at 45° C. it is practically nil.

The butylic bacillus of Fitz was isolated from amongst the products of the fermentation of glycerin, and in 1888[1] Morin had investigated its action, confirming the results already obtained by Fitz, as regards the production of the higher alcohols. The work of Perdrix on this subject is still more interesting. He had found, in the drinking water of Paris, a bacterium which appears to be none other than the bacillus of Fitz, and which gave from 105 to 110 c.c. of higher alcohols per kilo. of potatoes. When one remembers that potatoes contain about 200 grms. of starch per kilo., the yield works out to practically the same figure as is given by Fernbach and Strange in their patent, No. 448,364.

"Working under the conditions set forth above, it is possible to convert up to 50 per cent. of the carbohydrate employed into a mixture of acetone and higher alcohols."

This is what Perdrix did as regards the higher alcohols[2] in 1891.

Although he did not identify the ferment which gave him such results, with the butylic bacillus of Fitz employed by Fernbach, these two ferments seem to have a singular resemblance to one another, and appear to work under almost identical conditions.

"This bacterium," says Perdrix, "develops only out of contact with air, and is much better cultivated in an atmosphere of hydrogen or of carbonic acid. Its optimum temperature is 35° C., and the maximum should not exceed 43° C. Under favourable conditions the spores form completely in ten days; they differ from the *vibrio butyricus* of Pasteur, and from the amylobacters of Van Tieghem."

But what do Fernbach and Strange say as regards the process of fermentation?

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[1] *Comptes rendus*, 1887, 105, 816.

[2] *Zeit. f. Spirit. Ind.*, 1891, 14, 177.

"It has been found an advantage to carry out the fermentation in a closed vessel, connected with an aspirator and with a condenser, the aspirator being operated in such a manner as to obtain a reduction of pressure. . . . This reduction of pressure, with an aqueous wort, at a temperature of 30° to 40° C., should correspond to 150 mm. of mercury absolute."

If we set aside the use of degraded yeast, which Fernbach and Strange themselves admit to be unnecessary, the analogy between the two methods is rather striking, even down to the necessity of working in a medium devoid of air, at the identical temperatures of 30° to 40° C.

Further, Perdrix has suggested as advantageous the employment of an atmosphere of carbon dioxide, and despite the want of clearness in their description, Fernbach and Strange seem to have recourse to this also.

It is really astonishing, when these points of resemblance are considered, that Perdrix's work, although fairly well known, and referred to by Worden,[1] should have escaped the very thorough researches of Bliss, whom Perkin declares to have searched out everything relating to the problems investigated by Graham and Strange.

This property of converting starchy material into higher alcohols, more particularly butyl alcohol, does not appear to belong exclusively to the butylic bacillus of Fitz. On referring to Emmerling,[2] it will be found that *granulobacter butylicum* and *bacillus orthobutylicus* are also possessed of this valuable property, and form admirable auxiliaries for the synthesis of rubber, auxiliaries so much the more valuable because no one has dreamed of patenting their use, and they are, therefore, public property.

The analogy between the patent of Fernbach and Strange and anterior work does not, moreover, stop here. The method of procedure described by Pereire and Grignard[3] is not without resemblance to the degradation of yeast described in patent 448,364.

It is the same with Pringsheim's fusel oil bacillus,[4] a motile rod-shaped organism resembling Fitz's bacillus, which converts the potato into higher alcohols, producing at the same time carbon dioxide and hydrogen.

Thus, it seems to be demonstrated that the possibility of converting starchy material, or, better, sugars, into higher alcohols was known prior to Fernbach and Strange; in particular under the influence of Fitz's bacillus, under certain conditions already described by Perdrix; under the influence of *granulobacter butylicum* or *bacillus orthobutylicus;* and under the influence of Pringsheim's fusel oil bacillus. The rôle of these different organisms, and in particular of Fitz's *bacillus butylicus*, was, therefore, well known.

Consequently, the application of the latter ferment to the production of butyl alcohol does not appear to be so novel as Perkin would have it be understood.

Nevertheless it must, in all good faith, be admitted that the production of butyric acid accompanies, under certain circumstances—other than those examined by Perdrix—the conversion of the starchy material into butyl alcohol, and that numerous losses arise in this way.

It may be that it was with the idea of obviating this drawback that Fernbach and Strange introduced the companion process to the action of the bacillus of Fitz—viz., that of degraded yeast containing no proteins precipitable by tannin. There would be the new fact, and yet the possibility

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[1] *Nitrocellulose Industry*, vol. i., pp. 189-190.

[2] *Ber.*, 1904, 37, 3525.

[3] *J. Soc. pour l'Ind. Chim.*, 1902, 21, 558, 1090.

[4] *Ber.*, 1905, 38, 953.

of obtaining the results announced—that is to say, the conversion of starchy material into higher alcohols—even in the absence of degraded yeast, makes us a little sceptical on the point. It is known that yeast contains a certain amount of nitrogenous material which serves for its nutrition during the work of fermentation, and from which are derived the various amino-acids found in the vinasse residuals—such as leucin, isoleucin, butylalanine, asparagin, and glutaminic acid.

It is also known that Ehrlich has shown that on the fermentation of certain of these amino-acids, notably of leucin and isoleucin, depended the formation, in the manufacture of ethyl alcohol, of fusel oil.

What may occur on subjecting pressed yeast to the action of *tyrothrix tenuis* in a sterile medium, and after sterilisation ?

Tyrothrix tenuis is capable of fermenting albuminoid material.

It takes the form of small, slender rods, of fairly regular cylindrical shape, with a very slightly granular interior; these rods are about 0·6μ thick and of variable length, sometimes reaching 3μ.

Duclaux says that " it resembles the bacteria very strongly, exhibiting their rapidity of movement. It secretes rennet and casein, and acts upon nitrogenous matter, converting it into leucin and tyrosin. In this conversion there is concomitant formation of an ammonium salt of a fatty acid—viz., ammonium valerate."

Its power of converting the nitrogenous matter of yeast into leucin was undoubtedly responsible for its selection by Fernbach, for we know, from Ehrlich's work, that leucin is one of the compounds from which fusel oil is formed, and that if leucin be added to the starchy material undergoing fermentation the content of higher alcohols is largely increased. The same is true of butylalanine and of glutaminic acid. These conversions are represented by the following equations :—

(1) $(CH_3)_2CH \cdot CH_2 \cdot CH(NH_2) \cdot COOH + H_2O$

Leucin.

$\rightarrow (CH_3)_2CH \cdot CH_2 \cdot CH_2 \cdot OH + NH_3 + CO_2$

Isoamyl alcohol.

(2) $C_2H_5 \cdot CH(CH_3) \cdot CH(NH_2) \cdot COOH + H_2O$

Isoleucin.

$\rightarrow C_2H_5 \cdot CH(CH_3) \cdot CH_2 \cdot OH + NH_3 + CO_2$

Active amyl alcohol.

(3) $(CH_3)_2CH \cdot CH(NH_2) \cdot COOH + H_2O$

Butylalanine.

$\rightarrow (CH_3)_2CH \cdot CH_2 \cdot OH + NH_3 + CO_2$

Isobutyl alcohol.

(4) $CH_3 \cdot CH_2 \cdot CH(NH_2) \cdot COOH + H_2O$

Glutaminic acid.

$\rightarrow CH_3 \cdot CH_2 \cdot CH_2 \cdot OH + NH_3 + CO_2$

Propyl alcohol.

These reactions have already been explained at length, and there is no need to repeat the explanation. It will suffice to say that *tyrothrix tenuis* is capable of converting the nitrogenous matter of yeast into leucin, and that the latter yields isoamyl alcohol on fermentation.

It will, therefore, be easy to understand the very adroit selection of this ferment made by Fernbach for the purpose of degrading the yeast used in his process for the conversion of starchy matter into fusel oil.

On the other hand, *tyrothrix tenuis*, which acts powerfully on albuminoids, is without fermentative action on sugars; it could not, therefore, interfere with or modify the action of Fitz's bacillus, its power being exerted only on nitrogenous materials and not on carbohydrates. The resistance to heat of *tyrothrix tenuis* is remarkable. When heated in its early stages, within the first few hours of its development, in a neutral liquid, it is not destroyed until a temperature of 90° to 95° C. is reached; at the end of twenty-four hours, the liquid having become slightly alkaline, it resists a temperature of 100° C. perfectly.

In the form of well-formed spores, in an alkaline medium, it can even resist 115° C.; and lastly, it is between 25° and 35° C. that its growth is most rapid.

Although on reading Fernbach and Strange's patent specification it is perfectly easy to understand the formation of fusel oil, by the joint action of the Fitz bacillus and of *tyrothrix tenuis*, the one converting starch into butyl alcohol, as a number of chemists had already pointed out, the other converting nitrogenous matter into leucin, whence isoamyl alcohol—one of the constituents of fusel oil—is derived, it is much less easy to explain the formation of acetone, which, according to the text of the patent, constitutes one-third of the conversion products.

By what particular mechanism is the starch or dextrose converted into acetone? Is it a secondary action of Fitz's bacillus on butyl alcohol, or is it a still unknown property of *tyrothrix tenuis?*

The patent specification is silent on this point, and is content with establishing the presence of acetone among the fermentation products, without in any way indicating how it may originate. There is quite clearly insufficiency of description on this point.

During fermentation isopropyl alcohol must evidently be formed. Is the acetone formed by oxidation of this compound?

$$CH_3 \cdot CH(OH) \cdot CH_3 + O \rightarrow CH_3 \cdot CO \cdot CH_3 + H_2O.$$

In that case, whence is the necessary oxygen derived?

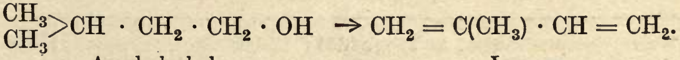
We do not doubt that Fernbach and Strange obtained acetone from starch under the conditions which they describe, but a little information about the process involved in this conversion instead of a simple statement of the result, would have made their patent clearer and more substantial.

Synthetic fusel oil being a product rich in butyl alcohol and poor in amyl alcohol, it can only serve as the raw material for butadiene, and short of methylating the latter, a costly operation, there can be no thought of obtaining isoprene from it.

The relationship connecting butadiene with butyl alcohol is the same as that which exists between amyl alcohol and isoprene:—

$$CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot OH \rightarrow CH_2 = CH \cdot CH = CH_2.$$

Butyl alcohol. Butadiene.



$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CH \cdot CH_2 \cdot CH_2 \cdot OH \rightarrow CH_2 = C(CH_3) \cdot CH = CH_2.$$

Amyl alcohol. Isoprene.

The method of preparation of the two hydrocarbons is, therefore, the same. The alcohol is converted into chloride by means of dry hydrogen chloride, and the chloride is then further chlorinated in the Pim apparatus, as has already been described.

The mixture of chlorobutanes produced gives on fractionation three principal dichlorides :—

(1) The 1·2 dichloride—$CH_3\cdot CH_2\cdot CHCl\cdot CH_2Cl$—boiling point, 125° C.
(2) „ 1·3 „ —$CH_3\cdot CHCl\cdot CH_2\cdot CH_2Cl$— „ 137° C.
(3) „ 1·4 „ —$CH_2Cl\cdot CH_2\cdot CH_2\cdot CH_2Cl$, with a very high boiling point.

When the vapours of these dichlorides are passed over soda lime heated to about 470° C., they all yield butadiene; consequently, it is useless to fractionate them.

The formation of erythrene from the 1·2 dichloride indicates that intramolecular change occurs on elimination of hydrogen chloride, since normally only the 1·3 and 1·4 dichlorides should give rise to butadiene.

The 1·3 dichloride may also be prepared from acetaldehyde, as explained later on. From this brief description it will be seen that the English synthesis comprises three processes :—

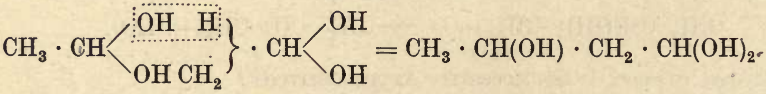
(1) Preparation of isoprene starting with isoamyl alcohol, which is converted into the dichloride, hydrogen chloride being then removed from the latter by means of soda lime.

(2) Preparation of butadiene from normal butyl alcohol by the same steps.

(3) Preparation of butadiene from acetaldehyde.

The aldehyde is condensed to alcohol by successive hydration and dehydration, according to the equations—

$$\underset{\text{Acetaldehyde.}}{CH_3\cdot CHO} + H_2O = \underset{\text{Ethanediol.}}{CH_3\cdot CH(OH)_2}.$$



$$CH_3\cdot CH\left\langle\begin{matrix}OH & H\\ OH & CH_2\end{matrix}\right\rangle\cdot CH\left\langle\begin{matrix}OH\\ OH\end{matrix}\right. = CH_3\cdot CH(OH)\cdot CH_2\cdot CH(OH)_2.$$

2 mols. ethanediol. Butanetriol.

$$\underset{\text{Butanetriol.}}{CH_3\cdot CH(OH)\cdot CH_2\cdot CH(OH)_2} = \underset{\text{Aldol.}}{CH_3\cdot CH(OH)\cdot CH_2\cdot CHO} + H_2O.$$

The union of two molecules of aldehyde to form an aldol may be brought about by the catalytic action of various substances, notably with an alkaline reaction,[1] such as NaOH, KOH in alcoholic solution, solid KOH, sodium acetate, and potassium and sodium carbonates.

It is advantageous to bring about condensation by means of a concentrated solution of potassium carbonate or bicarbonate.

The following method of operation has been described by Franke :—[2]

To 200 grms. of a saturated aqueous solution of potassium bicarbonate at 0° C., 200 grms. of acetaldehyde, also cooled to 0° C., is added in small

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[1] Wartz, *Comptes rendus*, 1872, 74, 1361; Lieben, *Monats.*, 1901, 22, 289.

[2] *Monats.*, 1906, 72, 909.

quantities at a time, care being taken that the temperature does not rise above 10° C. Solid potassium carbonate is then added to the mixture in sufficient quantity to bring about the separation of the liquid ~~into~~ two distinct layers, and the mixture is meanwhile shaken and kept cool. It is then allowed to stand for twelve hours in an ice-chest, after which it is extracted with ether.

The ethereal solution is accurately neutralised by the addition of dilute hydrochloric acid, washed with the smallest possible quantity of water, and dried by repeatedly pouring it through dry filters, and finally over freshly fused sodium sulphate. After distilling the ether the aldol is distilled *in vacuo*. It boils at 70° C. at 15 mm. pressure.

The yield of aldol is 55 per cent. of the weight of aldehyde taken.

During distillation partial depolymerisation into the original aldehyde always occurs. This aldehyde is absorbed by a column of strong sulphuric acid, in order to prevent reduction of the vacuum.

The freshly distilled aldol is a fairly mobile liquid, which changes rapidly into a thick oil with evolution of heat. This oil is extremely viscous, and after some time deposits crystals of paraldol.

In using magnesium amalgam in presence of benzene as condensing agent the amalgam reduces the aldol after it is formed, yielding butanediol, 1·3—[1]

$$CH_3 \cdot CH(OH) \cdot CH_2 \cdot CH_2 \cdot OH.$$

The same reduction may be effected either by the method of Sabatier and Senderens, or, better still, with sodium amalgam, or with magnesium obtained electrolytically in the Dubosc-Hermite apparatus. The alcohol—butanediol or butenylglycol—is converted into dichlorobutane, 1·3, by the action of hydrogen chloride under the usual conditions, and when dichlorobutane is heated at 400° C. with caustic soda, or, better still, with soda lime, it yields butadiene with loss of the elements of hydrogen chloride :—

$$CH_3 \cdot CHCl \cdot CH_2 \cdot CH_2Cl + 2NaOH = CH_2 : CH \cdot CH : CH_2 + 2NaCl + 2H_2O.$$

This process is fairly practical and fairly simple, having only a small number of stages, and in view of the fact that the dichlorobutane can be prepared by passing chlorine gas, in order to render it an industrial success it is necessary to be able to obtain acetaldehyde at a very low cost.

Acetaldehyde is obtained in the rectification of alcohol—when it is present in the first runnings—and also in the dry distillation of wood ; but on account of its very low boiling point (20° C.) it is hardly possible to condense it without the aid of a freezing mixture.

It is better to polymerise it, by the action of sulphuric acid, hydrogen chloride, zinc chloride, or anhydrous sodium acetate, to paraldehyde, which boils at 124° C., and which can afterwards be converted into acetaldehyde by heating it with a trace of sulphuric acid.

It may also be absorbed by sodium bisulphite, with which it forms a stable compound, and afterwards recovered by decomposing this compound with a strong acid.

Acetaldehyde may, again, be obtained by various classical processes, notably by the oxidation of ordinary alcohol.

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[1] Meunier, *Comptes rendus*, 1902, 134, 472; Tischtschenko and Grigoreew, *Centralbl.*, 1906, 2, 1555; Tischtschenko and Woronkow, *Centralbl.*, 1906, 2, 1556; Kling and Roy, *Comptes rendus*, 1907, 144, 1111.

Special attention must be drawn to the method of obtaining acetaldehyde by the hydration of acetylene, a gas easily prepared from calcium carbide.

The net result of this reaction is represented by the equation—

$$C_2H_2 + H_2O = CH_3 \cdot CHO.$$

When hydration is effected by the use of sulphuric acid, the acetaldehyde produced is at once condensed to crotonic aldehyde.[1]

Acetaldehyde itself can, however, be obtained by using dilute sulphuric (3 vols. H_2SO_4 to 7 vols. water) at the boiling point, together with a little mercuric oxide.[2]

The mercuric oxide plays a special part in this reaction, an intermediate compound being formed which can be isolated.

If a current of acetylene gas, purified by passing it through solutions of caustic soda, iron sulphate, and calcium chloride, be passed into a solution of a mercury salt—dichloride or nitrate, for example—the gas is rapidly absorbed, and a bulky precipitate is formed so long as any free mercuric salt remains. The same thing occurs with substituted acetylenes, including allylene, $CH_3 \cdot C \vdots CH$, and allene, $CH_2 : C : CH_2$, which both give the same precipitate.[3] Moreover, the product formed is not an acetylide, analogous to those obtained with copper and silver salts, or the alkaline solutions of mercury salts, such as Nessler's reagent (with which allylene gives a precipitate of $(CH_3 \cdot C \vdots C)_2Hg$, whilst allene does not react).

If the precipitate be suspended in acidified water and heated to boiling, it is decomposed into the original mercury salt, and not the acetylene hydrocarbon, but its hydrate—in the case of acetylene, acetaldehyde. Other acetylene hydrocarbons yield ketones.[4] Allylene and allene, for example, yield ordinary acetone.

The reaction, if carefully carried out, goes quantitatively, a molecule of acetylene giving a molecule of acetaldehyde, and the mercuric salt being completely regenerated, in a condition in which it is ready to react with a similar quantity of acetylene, and transform it into acetaldehyde. The aldehyde is collected, as formed, in a receiver kept at a temperature below 0° C., or is converted either into the more stable paraldehyde, or the bisulphite compound.

The white precipitate formed when acetylene is passed into a solution of mercuric chloride was formerly regarded as an addition product.

It has since been recognised that it is a mercuric derivative of aldehyde, or of a ketone, in the case of the substituted acetylenes.

With acetylene itself trichloromercurialdehyde is formed—

$$C_2H_2 + 3HgCl_2 + H_2O = C(HgCl)_3 \cdot CHO + 3HCl.$$

Similarly, allylene gives trichloromercuriacetone, $CH_3 \cdot CO \cdot C(HgCl)_3$.

When these compounds are heated in presence of acid, mercuric chloride and acetaldehyde (or the corresponding ketone) are formed—

$$C(HgCl)_3 \cdot CHO + 3HCl = 3HgCl_2 + CH_3 \cdot CHO.$$

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[1] Berthelot, *Comptes rendus*, 1862, 50, 805; Lagermark and Eltekow, *Ber.*, 1877, 10, 637.

[2] Erdmann and Koethner, *Zeit. anorg. Chem.*, 1898, 18, 48.

[3] Lossen and Dorno, *Ann.*, 1905, 342, 184, 189.

[4] Kutscheroff, *Ber.*, 1884, 17, 13; K. A. Hofmann, *Ber.*, 1899, 32, 874; 1904, 37, 4449; Biltz and Rumna, *Ber.*, 1904, 37, 4417.

Berger and Reychler state that the conversion of acetylene into acetaldehyde does not go well when the liquid is strongly acid; on the other hand, it is necessary to avoid excess of alkali, otherwise the trichloromercuriacetaldehyde will be converted into mercury acetylide, which is explosive at 23° C. When a few precautions are taken this process goes very smoothly, and may be worked continuously if the source of acetylene be connected to two mercury absorbers, which can be heated. The one serves for the preparation of trichloromercuric acetaldehyde, by absorbing the current of gas, whilst the other, on heating, yields acetaldehyde, the mercury salt being regenerated. A method such as this used in the preparation of butadiene allows of the production of a material, at a very low price, which can easily compete with butyl alcohol.

Admitting that the yields are only 50 per cent., the consumption of calcium carbide would be about 4 lbs. per lb. of rubber, representing an outlay of about 3¾d. in raw material. Under the same conditions, also assuming a yield of 50 per cent. with butyl alcohol at the price given by Perkin—viz., 5d. per lb.—and the consumption being 2·7 lbs., the cost would be 1s. 6d. per lb. of rubber.

The calcium carbide-acetaldehyde process seems, then, to be one of those which are apparently of the greatest interest, from the economic point of view; but from the technical standpoint it will offer certain difficulties in manipulation.

To conclude this account of the processes of the second group a method patented by Bayer[1] must be mentioned; this is based on the condensation of acetone with formaldehyde in presence of weak bases; keto-2-butanol is thus obtained—

$$CH_3 \cdot CO \cdot CH_3 + CH_2 : O = CH_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot OH.$$

On removing a molecule of water from this keto-alcohol, methylene acetone is obtained—

$$CH_3 \cdot CO \cdot CH : CH_2,$$

which, when methylated by means of organo-magnesium compounds, gives isoprenic alcohol, from which, in turn, isoprene can readily be obtained by one of the methods already described. Ostromyslensky's method may also be classed in the second group, although it is rather a regeneration of rubber than a preparation, properly so-called. It consists in converting caoutchouc into bromide, in the ordinary way, then removing from it the elements of hydrogen bromide, by means of alcoholic alkalies, or amines at a high temperature. The effect is other than that described by Weber, in which the bromine atoms are replaced by phenolic groups.

Merling and Hugo Kohler, lastly, treat isopropenylmethyl carbinol with a dehydrating agent, such as oxalic acid, and obtain isoprene. In another process they replace the hydroxyl group of isopropenylmethyl carbinol by a halogen atom, and treat the halogen derivative with an agent capable of dissolving it.

For example, the hydroxyl group may be replaced by chlorine, and the chlorine derivative treated with alcoholic alkali.

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[1] Ger. Pat. 222,623 (2), C. 12, I., p. 385.

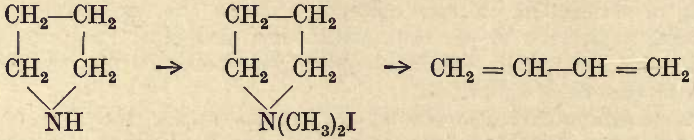
CHAPTER XIV.

METHODS OF PREPARING ISOPRENE AND ITS HOMOLOGUES.

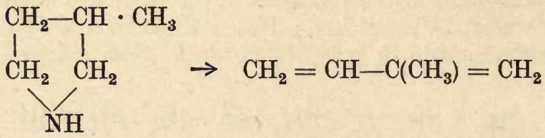
(*Continued*).

Methods of Group 3—Use of Nitrogen Bases.—We include in this group all those reactions in which the synthesis of homologues of erythrene is effected with the aid of organic bases.

Ciamician and Magnaghi[1] obtained butadiene by exhaustive methylation of pyrrolidine, followed by decomposition of the methiodide with alcoholic potash—

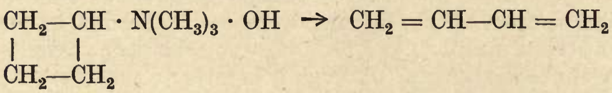


By an analogous process, Euler[2] obtained isoprene starting with β-methyl pyrrolidine.



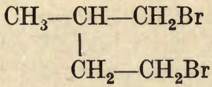
These syntheses are of purely theoretical interest, for the quantity of isoprene obtained did not exceed 2 grms.

Willstätter and Von Schmœdel[3] also obtained erythrene, starting with the following quaternary ammonium hydrate—



$$\begin{array}{l} CH_2\text{—}CH \cdot N(CH_3)_3 \cdot OH \\ |\quad\quad\ | \\ CH_2\text{—}CH_2 \end{array} \rightarrow CH_2 = CH\text{—}CH = CH_2$$

Harries and Neresheimer,[4] adopting a method which has already been mentioned under the second group, started with the dibromide of β-methyltetramethylene—



$$\begin{array}{l} CH_3\text{—}CH\text{—}CH_2Br \\ \quad\quad\ | \\ \quad\quad CH_2\text{—}CH_2Br \end{array}$$

obtained from β-methyltetramethylene glycol, and heated it in a sealed tube with a 33 per cent. solution of trimethylamine in absolute alcohol for three hours at 100° C. After carefully evaporating the product *in vacuo* they obtained a heavy, viscous, yellowish mass, consisting of the bis-quaternary bromide.

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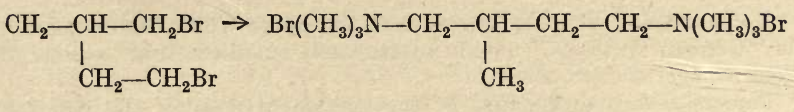
[1] *Gaz. Chim. Ital.*, 1895, 15, 485.

[2] *Ber.*, 1897, 36, 1989.

[3] *Ber.*, 1905, 38, 1992.

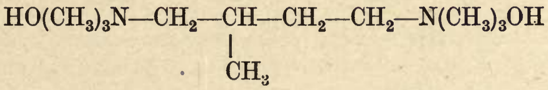
[4] *Annalen*, 1911, 383, 157.



$$CH_2{-}\underset{\displaystyle CH_2{-}CH_2Br}{\overset{}{\underset{|}{CH}}}{-}CH_2Br \rightarrow Br(CH_3)_3N{-}CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CH_2{-}CH_2{-}N(CH_3)_3Br$$

This compound is soluble in water, ethyl alcohol, and methyl alcohol; it is insoluble in ether, light petroleum, and benzene. It cannot be obtained crystalline, and it could not be completely purified.

It was dissolved in water, and treated with twice the calculated amount of moist silver oxide; the reaction sets in at once, and is completed by frequent agitation. The silver bromide and excess of silver oxide are filtered off, and the strongly alkaline filtrate is evaporated *in vacuo*. The bis-quaternary base is thus obtained in the form of a viscous liquid, coloured greyish-blue by traces of silver salt.



$$HO(CH_3)_3N{-}CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CH_2{-}CH_2{-}N(CH_3)_3OH$$

The product distils, with much frothing, beginning at 100° C., and leaving behind only a small residue.[1] The vapour is condensed in a short condenser, and then passes a second distilling flask, which is not cooled, and in which water and the greater part of the trimethylamine condense, the latter in solution, whilst the isoprene, insoluble and volatile, is collected in a condenser cooled to 0° C. by means of a freezing mixture.

When distillation is at an end the first receiver is heated for some time on the water-bath at 50° C., in order to drive over into the second the small amount of isoprene which it may contain. The trimethylamine is then taken up with well-cooled dilute sulphuric acid.

The isoprene is rectified again over sodium on the water-bath, the greater part passing over between 36° and 37° C., whilst the remainder boils at 50° C. The yield is about 50 per cent. The change is represented by

$$\underset{\text{Base}}{HO(CH_3)_3N \cdot CH_2 \cdot CH(CH_3) \cdot CH_2 \cdot CH_2 \cdot N(CH_3)_3 \cdot OH}$$

$$= \underset{\text{Isoprene.}}{CH_2 : CH(CH_3) \cdot CH : CH_2} + \underset{\text{Trimethylamine.}}{2N(CH_3)_3} + 2H_2O.$$

The optical constants of the product thus obtained are as follows:—

$$n_D^{21°} = 51 \cdot 1° ; \qquad n_D^{21°} = 1 \cdot 42267$$

$$C_\alpha^{21°} = 51° ; \qquad n_\alpha^{21°} = 1 \cdot 41807$$

$$i_\gamma^{21°} = 52 \cdot 5° ; \qquad n_\gamma^{21°} = 1 \cdot 44340$$

$$d_{21°}^{21°} = 0 \cdot 6804 ; \qquad d_{4°}^{21°} = 0 \cdot 6793$$

$$M_D \text{ (calc.)} = 24 \cdot 33, \text{ (found)} = 25 \cdot 45$$

$$M_\gamma - M_\alpha \text{ (calc.)} = 0 \cdot 94 ; \text{ (found)} = 1 \cdot 33$$

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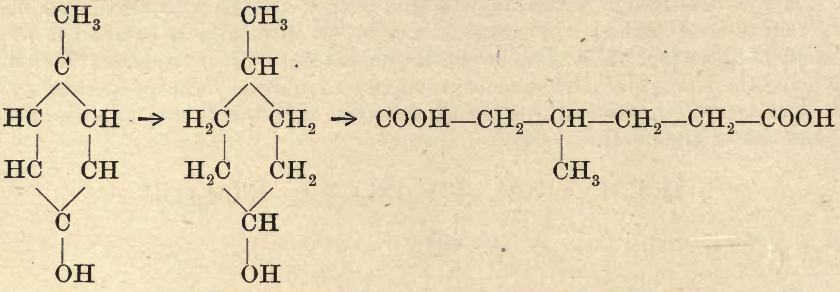
[1] Elberfeld, Ger. Pat. 231,806.

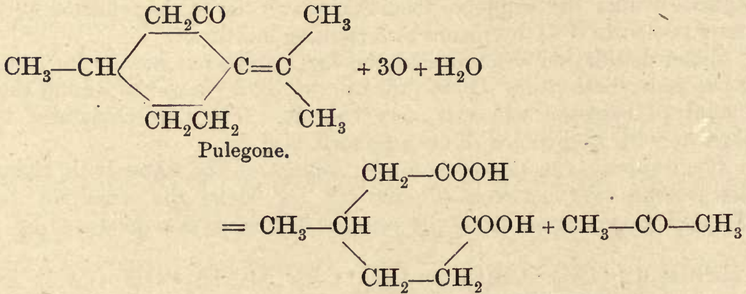
Hoffmann and Coutelle, chemists of the Bayer Works, who worked out the "German synthesis," obtain isoprene and butadiene from coal-tar products—viz., cresol and phenol.

Paracresol is hydrogenated by the method of Sabatier and Senderens, by passing a mixture of its vapour and hydrogen over reduced nickel. Methylcyclohexanol is thus formed, and this compound yields, on oxidation, β-methyladipic acid, the benzene ring being opened.



p-cresol. *p*-methylcyclohexanol. β-methyladipic acid.

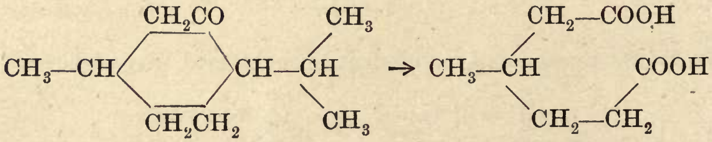
β-methyladipic acid is a well-known substance in the chemistry of the terpenes. It is obtained when pulegone is oxidised by permanganate—



Pulegone.

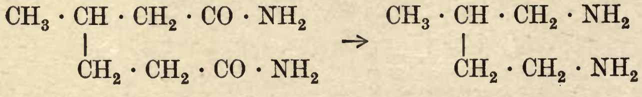
β-methyladipic acid.

Menthone behaves in a similar way—



Menthone. β-methyladipic acid.

Returning to the Bayer synthesis, the diamide of β-methyladipic acid is converted by Hoffmann's method—by means of hypochlorous acid—into β-methyltetramethylenediamine—



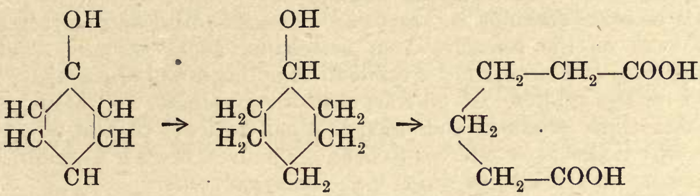
$$\begin{array}{l} \mathrm{CH_3 \cdot CH \cdot CH_2 \cdot CO \cdot NH_2} \\ \quad\ \ | \\ \quad\ \ \mathrm{CH_2 \cdot CH_2 \cdot CO \cdot NH_2} \end{array} \rightarrow \begin{array}{l} \mathrm{CH_3 \cdot CH \cdot CH_2 \cdot NH_2} \\ \quad\ \ | \\ \quad\ \ \mathrm{CH_2 \cdot CH_2 \cdot NH_2} \end{array}$$

which on exhaustive methylation yields a very pure isoprene.

Harries states that he has examined this process, and finds that it works well.

The only criticism that can be brought against it is that it is necessary to employ expensive processes, such as hydrogenation and methylation.

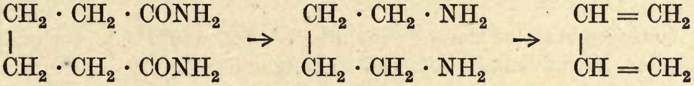
If phenol be employed instead of *p*-cresol, butadiene is obtained, the reaction proceeding through the compounds cyclohexanol and adipic acid—



The conversion of cyclohexanol into adipic acid by oxidation is very simple.

Using, as oxidising agent, pure nitric acid, and heating, a yield of 295 grms. of adipic acid is obtained from 300 grms. of cyclohexanol.[1] The oxidation may also be effected by means of permanganate.[2]

To a solution of 120 grms. of crystalline sodium carbonate in a litre of water, 60 grms. of cyclohexanol is added, and, to the mixture, a solution of 270 grms. of permanganate in 5 litres of water, with frequent shaking. After three days the manganese dioxide is filtered off at the pump, the filtrate is concentrated to 500 c.c. in volume, and the adipic acid is then liberated by the addition of concentrated hydrochloric acid. The diamide of adipic acid is prepared, and from it, tetramethylenediamine. The latter is then exhaustively methylated, and treated with an alkali[3] or with silver oxide,[4] when butadiene is obtained—



$$\begin{array}{c} CH_2\cdot CH_2\cdot CONH_2\\ | \\ CH_2\cdot CH_2\cdot CONH_2 \end{array} \rightarrow \begin{array}{c} CH_2\cdot CH_2\cdot NH_2\\ | \\ CH_2\cdot CH_2\cdot NH_2 \end{array} \rightarrow \begin{array}{c} CH = CH_2\\ | \\ CH = CH_2 \end{array}$$

Adipic diamide. Tetramethylenediamine. Butadiene.

Although it is impossible to avoid the methylation process, with the inevitably great losses which accompany it, and the cost cannot, therefore, be reduced at this stage, the process of hydrogenation can be carried out to-day under fairly practical conditions. Hydrogen can be prepared by d'Arsonval's process, which consists in separating from coal-gas all the constituents except hydrogen by cooling with liquid air; it may also be obtained by Majert and Richter's process, from zinc dust and lime; by the electrolytic methods of Schakert, Garrati and Schmidt, and Meuricheau-Beaupré (who employs aluminium filings), and especially by Jaubert's method, by which hydrogen is obtained, at very low cost, by the action of ferro-silicon on soda—

$$Si + Ca(OH)_2 + 2NaOH = Na_2O, SiO_2, CaO + 2H_2$$

---

[1] Bouveault and Locquin, *Bull. Soc. Chim.*, 1908, 3, 437.
[2] Mannich and Hâncu, *Ber.*, 1908, 41, 575.
[3] U.S. Pat. 1,028,938, June 11, 1912.
[4] U.S. Pat. 1,005,217, Oct. 10, 1911.

Jaubert's hydrolith, or hydrogenite, may also be used as a source of hydrogen at a very reasonable cost.

Instead of starting with coal-tar derivatives, such as phenol, cresol, or xylenol, and reducing these compounds, which involves a somewhat delicate operation, one may, with advantage, start with petroleum products, which on oxidation with fuming nitric acid can be made to yield adipic acid in abundance, and at a much lower cost.

This reaction does not appear to have been studied, and neither Harries, in his work on the pentanes from petroleum, nor Perkin, in speaking of investigations of a similar order carried out by his group of chemists, breathe a word on the subject. It may be that the possibility of obtaining adipic acid from these products had escaped their notice; that is all the more reason why it should be referred to here. Moreover, there is a certain amount of literature on the subject which we propose to quote.

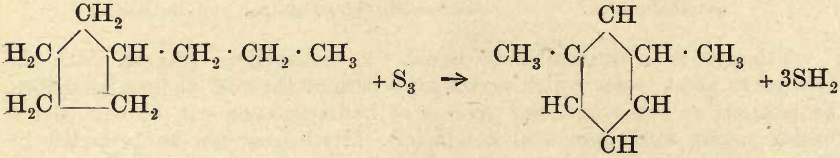
According to the work of Markownikoff[1] and Oglobin, Caucasian petroleum, and in particular that from the Apscheron Peninsula, is a mixture of saturated hydrocarbons of the general formula C_nH_{2n}. The wastage resulting from the acid treatment of these hydrocarbons amounts to 50,000 tons, and that from the soda treatment to 30,000 tons per annum.

These hydrocarbons constitute the class of chemical compounds called naphthenes, and form a very complex mixture, separable by fractional distillation. In the mixture are found—

(1) Hexahydrobenzene derivatives,
(2) Pentamethylene derivatives,
(3) Hexamethylene derivatives,

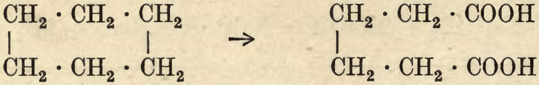
all of which are interesting substances to study, from the standpoint of the preparation of raw material for the various synthetic rubbers, and which up to now seem to have been overlooked, in spite of their abundance and their low cost.

On heating certain of these hydrocarbons—octonaphthene, for example—with sulphur, Markownikoff obtained metaxylene:—



This substance may be of interest in the case which we are considering.

Aschan[2] has studied the cyclohexane present in the fraction described as "petroleum ether," and boiling between 78° and 82° C., of Hanoverian, Galician, and Caucasian petroleum. Cyclohexane is attacked only with difficulty, and can only be converted into adipic acid by the prolonged action of nitric acid—



Cyclohexane. Adipic acid.

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[1] *Ber.*, 1893, 26, 370.

[2] See on this subject the book by Wischin, *Die Naphthene*, published by Vieweg u. Sohn; also Aschan, *Ber.*, 1899, 32, 1771.

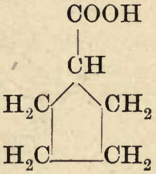
As hexanaphthene contains a little pentamethylene a certain amount of glutaric acid is formed at the same time, and constitutes an impurity—

Pentamethylene. Glutaric acid.

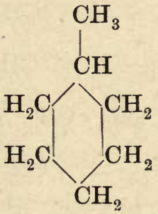
By the action of chlorine the pentamethylene ring is broken, and halogen derivatives are formed. The reaction is extremely violent, and, in sunlight, may even become explosive. The chloro-compounds yield unsaturated hydrocarbons when treated with metallic oxides, quinoline, or sodium acetate.

It would be of extreme interest to take up the study of these compounds, in order to see whether it is not possible to obtain from them either butadiene or isoprene, as from the number of carbon atoms in their chain might well be the case.

In addition to the hexanes and pentanes, there are also present certain acids, the naphthenic acids, which have the general formula $C_nH_{2n-2}O_2$, and are carboxylic acids containing 5-carbon rings—



These may also be of use for our special purpose. In another fraction, distilling at about 120° C., methylcyclohexane, C_7H_{14}, or heptanaphthene, is found—



This compound is identical with the hexahydrotoluene, discovered by Wreden in resin oils, and which can be used in processes of the first group for the production of isoprene. Were it only as a source of adipic acid, these petroleum products would be extremely interesting, for oxidation of the hexamethylenes yields this acid in a much simpler way than the hydrogenation of phenol by the method of Sabatier and Senderens.[1]

The isoprene and butadiene, obtained from β-methyladipic acid, and adipic acid respectively, are extremely pure; the isoprene, notably, has

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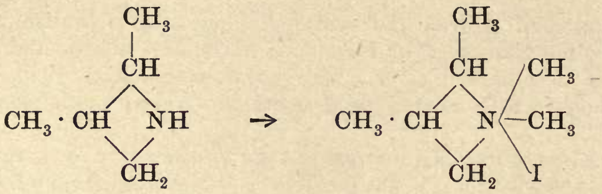
[1] Adipic acid may also be obtained by the oxidation, by means of nitric acid, of sebacic acid (Laurent), or of castor oil (Dieterle), or by oxidising cyclohexanone in the cold, with permanganate and sodium carbonate (Mayer).

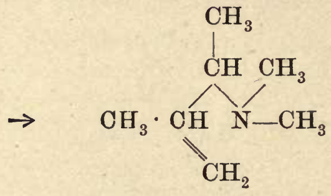
the same physical constants as the product prepared by Harries and Neresheimer from β-methyltetramethylene.

The Bayer works have applied for a number of patents, which may be classified in the third group, and which have as their object the preparation of erythrene or isoprene.

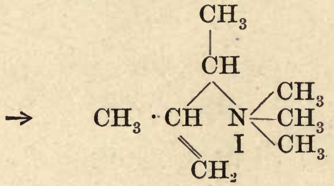
By the action of methyl chloride or iodide on α-β-dimethyltrimethyleneimine, the haloid salt of α-β-dimethyltrimethylenedimethylammonium is obtained.[1]



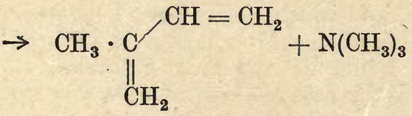
This substituted ammonium haloid is converted in α-β-dimethylallyldimethylamine either by the action of moist silver oxide, followed by distillation, or by heating with powdered caustic potash—



The amine thus obtained is converted into α-β-dimethylallyltrimethylammonium iodide by the action of methyl iodide :—



which with powdered caustic potash gives isoprene and trimethylamine—



In a quite analogous manner, α-methyltrimethyleneimine will give rise to erythrene.

In another process[2] the Bayer works convert into isoprene and butadiene

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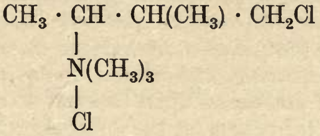
[1] Ger. Pat. 31,662.

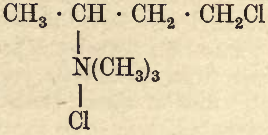
[2] Ger. Pat. 31,722.

respectively the chlorides and iodides of the substituted ammoniums containing halogen, having the formulæ



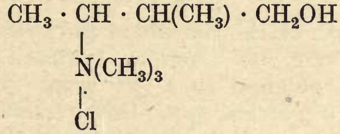
$$\begin{array}{l} CH_3\cdot CH\cdot CH(CH_3)\cdot CH_2Cl \\ \qquad\ | \\ \qquad N(CH_3)_3 \\ \qquad\ | \\ \qquad Cl \end{array}$$

and



$$\begin{array}{l} CH_3\cdot CH\cdot CH_2\cdot CH_2Cl \\ \qquad\ | \\ \qquad N(CH_3)_3 \\ \qquad\ | \\ \qquad Cl \end{array}$$

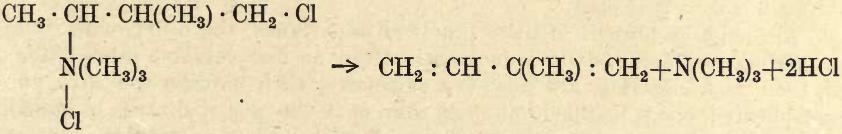
The former of these, used in preparing isoprene, is obtained by saturating the corresponding hydroxy compound



$$\begin{array}{l} CH_3\cdot CH\cdot CH(CH_3)\cdot CH_2OH \\ \qquad\ | \\ \qquad N(CH_3)_3 \\ \qquad\ | \\ \qquad Cl \end{array}$$

with hydrogen chloride.

The chloro-substituted ammonium chloride yields isoprene and trimethylamine by the action of caustic alkali—either solid, or in concentrated solution—or of lime or caustic baryta—



$$\begin{array}{l} CH_3\cdot CH\cdot CH(CH_3)\cdot CH_2\cdot Cl \\ \qquad\ | \\ \qquad N(CH_3)_3 \qquad\qquad \rightarrow\ CH_2 : CH\cdot C(CH_3) : CH_2 + N(CH_3)_3 + 2HCl \\ \qquad\ | \\ \qquad Cl \end{array}$$

A last process[1] concerns the use of substituted ammonium chlorides of the following constitution :—

$$CH_3\cdot CHCl\cdot CH(CH_3)\cdot CH_2\cdot N(CH_3)_3\cdot Cl$$

and $CH_3\cdot CHCl\cdot CH_2\cdot CH_2\cdot N(CH_3)_3\cdot Cl.$

The former of these two chlorides, which is the starting point for the preparation of isoprene, is obtained by the addition of methyl chloride to the hydroxy-base—

$$CH_3\cdot CH(OH)\cdot CH(CH_3)\cdot CH_2\cdot N(CH_3)_3$$

and the treatment of the compound obtained with hydrogen chloride.

This chloro-chloride is decomposed by powdered caustic potash, or barium hydrate almost quantitatively into isoprene and trimethylamine :—

$$CH_3\cdot CHCl\cdot CH(CH_3)\cdot CH_2\cdot N(CH_3)_3Cl$$
$$\rightarrow\ CH_2 : CH\cdot C(CH_3) : CH + N(CH_3)_3 + 2HCl.$$

Butadiene can again be obtained, starting with cyclobutylamine, by treating this compound with phosphoric acid, crystallising the product, and heating it at 200° C.

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[1] Ger. Pat. 31,713.

Of the whole series of synthetic processes which have now been described, the number of those which are capable of immediate practical application is very small, practically only those based upon coal-tar (phenol and cresol), starch (isoamyl and butyl alcohols), calcium carbide (aldehyde, acetic acid, acetone, pinacone), petroleum products (adipic acid, or halogen-isopentanes), or residues from distilleries, sugar refineries, and starch mills (synthetic fusel oils). And of these, those which are based upon the use of starch or calcium carbide appear to be superior to the others for the following reasons :—

(1) The low cost of the raw materials.
(2) The low cost of the auxiliary materials.
(3) The small number and the simplicity of the stages in the process.

It is this, moreover, which constitutes the evident superiority of the "English synthesis" over the "German synthesis"—even if the latter start with adipic acid obtained from petroleum—provided the Fernbach process really works in a practical way. In the German synthesis the stages are, in fact, too numerous, and the exhaustive methylation of tetramethylene diamine is too expensive a process.

In our opinion the future at present seems to belong either to the higher alcohols—isoamyl and butyl—employed by Perkin and his collaborators, or to acetaldehyde, obtained from calcium carbide, provided the preparation of aldol can be perfected.

Although at present of little practical importance, the other methods of preparing isoprene and its homologues afford no less valuable information; if their raw materials are now too expensive, their process too slow and complicated, one is justified in hoping that, as in the case of alizarin, of indigo, and of camphor, simplifications will be effected, and costs reduced, so that synthetic rubbers may advantageously enter upon the struggle with natural rubbers.

CHAPTER XV.

THE PREPARATION OF SYNTHETIC RUBBER.

Polymerisation of Isoprene and Its Homologues.—In the synthesis of rubber, chemistry, as in many analogous cases, has gone beyond nature. The polymerisation of isoprene has, in fact, yielded—as Bouchardat, with intuitive genius, foresaw—a rubber similar to the natural product; but beyond this, by applying the same methods to the higher or lower homologues of isoprene—viz., butadiene and dimethylbutadiene—products similar to rubber, although not hitherto found in nature, have been obtained. There should be nothing astonishing in this, since the same thing had already happened in the case of the sugars.

The amount of work done on polymerisation as applied to the preparation of synthetic rubber, is very extensive, and we shall deal with it in chronological order.

The first chemist who, after having analysed the rubber complex as completely as was possible in his day, attempted to complete his chemical work by a synthesis, and was successful, was François Gustave Bouchardat.

There is universal agreement on this point; Harries and Perkin, Kondakow and Duisberg, all pay homage to him, and regard him as the father of synthetic rubber.

Harries says[1]:—" Bouchardat had the boldness to conceive of a direct relationship between isoprene, of which only very small quantities are formed in the dry distillation of rubber, and the latter substance. I regard it as a remarkable fact that he should have described as rubber the mass formed by the polymerisation of isoprene, although he had no means of demonstrating this experimentally."

Moreover, Harries has not hesitated to take advantage of repeated opportunities to pay tribute, with a sincerity which should be emphasised, to the inductive power and the far-sighted genius of the French savant. This confession is too valuable to be forgotten.

Perkin,[2] although less definite and precise, recognises the great importance of Bouchardat's work, but passing over in silence a large number of his investigations, he seeks to attribute either to Greville Williams or to Tilden, his fellow-countrymen, the more important rôle in the synthesis with which we are concerned. Referring to the bibliographic work, somewhat incomplete, carried out by his colleague, Bliss, he says:—" It is of the greatest interest to note that it was an Englishman, Greville Williams, who, in 1860, was the first to isolate isoprene, from among the products of the distillation of rubber, in a high state of purity, and that to him also is due the announcement of the conversion of isoprene into a substance analogous to rubber."

On this particular point Perkin seems not to have been acquainted with the work of Appolinaire Bouchardat, the father of the discoverer of the synthesis.

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[1] *Gummi Zeit.*, 1908, 33, 159.

[2] *J. Soc. Chem. Ind.*, 1912, 31, 616.

Perkin continues :—" Greville Williams found that when isoprene is kept it becomes viscous, and acquires oxidising properties ; as he remarks, it is ozonised. On distilling this ozonised isoprene, some unchanged hydrocarbon first passes over, and then the liquid thickens and the boiling point rises rapidly ; a vigorous reaction next takes place, fumes being given off, accompanied by a penetrating odour.

" The contents of the retort," says Greville Williams,[1] " solidify at once to a white spongy mass, which, if it has been properly prepared, scarcely sticks to the fingers. When it is pure it is opaque, but when exposed to the air, especially when warm, it becomes transparent, first of all at the edges, then throughout the mass. When burned it emits a peculiar odour, which has hitherto been regarded as characteristic of rubber itself. It is certain that Greville Williams had at his disposal an insufficient quantity of this substance, in the pure state, to be able to identify it definitely as rubber, which it undoubtedly contained, but it is clear, from various remarks made by him, that he regarded both gutta-percha and rubber as polymerides of isoprene."

These ideas of Greville Williams must have been adopted by Heinemann [2] fifty-five years later, when he treated isoprene with oxygen or ozone, and heated it until it became viscous.

" In 1875," Perkin continues, " Bouchardat examined the products of distillation of rubber, and also arrived at the conclusion that the substances obtained by condensation—such as dipentene, $C_{10}H_{16}$, or caoutchine—were polymerides of isoprene.

" He showed that isoprene is converted, on heating in a sealed tube, into a mixture of terpenic compounds, and a badly defined substance, called colophene, which without doubt contained rubber.

" In 1879, the same author showed that a relationship exists between turpentine and di-isoprene, definitely connecting isoprene with the terpenes.

" The same year, when preparing isoprene hydrochloride, he found that this hydrocarbon combines with a saturated solution of hydrogen chloride, but, on attempting to distil the hydrochlorides, he found that a portion remained as a solid residue in the flask.

" Examination of this residue showed it to be elastic and to possess the other properties of rubber, and to be insoluble in alcohol, but to swell up in ether and carbon disulphide, in which it gradually dissolved in the manner of natural rubber. This product gave on dry distillation the same volatile hydrocarbons as rubber."

Duisberg, in lecturing before the Congress of Applied Chemistry in New York, 1912, said :—

" It was the French chemist, Bouchardat, who was the first to express the view that isoprene, which he had obtained in a very small quantity, and in a very impure state, by the dry distillation of rubber, might be intimately and closely related to rubber."

Kondakow, whilst acknowledging with rather bad grace the priority of Bouchardat's synthesis of rubber, says that, although he may have obtained a result by using hydrochloric acid as a condensing agent, that is due to the fact that he was dealing with isoprene which had been exposed to light,

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[1] *Phil. Trans.*, 1860, 150, 254 ; *Proc. Roy. Soc.*, 1860, 10, 516.

[2] Eng. Pat. 14,041 of 1910.

and which, as he (Kondakow) has shown, does not behave in the same way as when freshly prepared.

The part played by the French chemist was greater than Kondakow is willing to recognise, and in order to obtain a complete knowledge of it, it is only necessary to refer to the various papers which have appeared in the *Bulletin de la Société Chimique*,[1] in which Bouchardat has described, with great modesty and simplicity, the work which led him up to a complete synthesis of rubber.

At the suggestion of Berthelot, in whose laboratory he was working, Bouchardat took up the work begun by his father, Appolinaire Bouchardat, and by Greville Williams, on the products of decomposition by heat of rubber. In 1875 he succeeded in condensing isoprene to dipentene; in 1882, by the use of hydrochloric acid, he obtained caoutchouc from the same hemiterpene.

By heating isoprene with dilute acids, he obtained an elastic product, which, after treatment with boiling water, possessed all the physical properties of rubber, and on dry distillation yielded, amongst other substances, isoprene and dipentene. He writes :—

" The method employed is as follows :—A certain quantity of isoprene is subjected to the action of five times its own weight of concentrated hydrochloric acid in a sealed tube, the tubes being placed in a freezing mixture. If, after a few moments, the tubes are shaken, a violent reaction, accompanied by considerable liberation of heat, occurs. The mass thus obtained is allowed to stand for several weeks, and shaken occasionally. On then fractionally distilling it, after dilution with water, the following products are obtained :—

" (1) Isoprene monohydrochloride—C_5H_8HCl.

" (2) Isoprene dihydrochloride—C_5H_8, 2HCl.

" (3) A solid residue, which, when freed, by means of boiling water, from the hydrochlorides with which it is contaminated, has the following composition :—$C = 87{\cdot}1$, $H = 11{\cdot}7$, $Cl = 1{\cdot}7$ per cent.

" Neglecting the chlorine, which arises from the partial decomposition of the hydrochlorides by water, and from which the mass can only be freed with difficulty, its elementary composition shows that one is dealing with a substance analogous to natural caoutchouc. It is insoluble in water, but swells up in ether and in carbon disulphide; it dissolves in the distillation products of Para rubber, and, lastly, on heating it yields the same products as rubber—viz., isoprene, caoutchine, dipentene, eupione, heveene."

It must be admitted that this description is a model of brevity and clearness. No detail is missing, yet the various points are made succinctly, in the fewest possible words.

This synthesis, which should have created a great stir, and made the name of its author famous, remained almost unknown outside a circle of scientific men, and persons interested in rubber from a practical point of view. It is correct to say that in 1882 the automobile did not exist, the bicycle had only just arrived, and the enormous expansion before the rubber industry could not be foreseen.

Opposed to self-advertisement, Bouchardat continued his work quietly, regardless of a discovery which might revolutionise from top to bottom an industry in which a capital of more than forty million pounds sterling was concerned, constituting indeed one of the greatest of the world's industries.

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[1] 1875, 24, 108, 111; *Comptes rendus*, 1879, 89, 361, 1117.

Tilden took up Bouchardat's work as much from the point of view of the preparation of isoprene as from that of the synthesis of rubber.

We have given a brief account of the first investigation elsewhere.

Perkin has given a very lucid account of the second, in the following words :—

"In 1882 Tilden[1] wrote : 'Isoprene has two characteristics which distinguish it from the terpenes. One is its curious property of exploding when, on exposure to air, it is converted into a white syrupy substance ; the other is the singular transformation of this hydrocarbon into actual rubber when it is brought into contact with certain chemical reagents, as, for example, concentrated hydrochloric acid (already observed by Bouchardat), or nitrosyl chloride.' "

In 1888 Tilden[2] published a paper on the decomposition by heat of turpentine, in which he showed that isoprene, one of the constituents of the distillate, can be converted into rubber. This was the first synthesis, starting from a substance other than the polyterpene itself. This investigation is of special interest, for it shows that Tilden at this time, long before the "German synthesis" foresaw the possibility of industrialising both his own discoveries and those of Bouchardat.

He says :—"The action of hydrochloric acid on isoprene converts it partially into caoutchouc ; the latter seems to be obtained more easily starting with the oily polymeride resulting from the action of heat. Contact with a cold concentrated acid brings about the same transformation."

Tilden, again, puts forward the following hypothesis :—"In the same way as isoprene polymerises to form terpenes, a group to which caoutchouc and gutta belong, so should the homologues of isoprene, C_4H_6, C_6H_{10}, C_7H_{12}, be capable of polymerisation to a series of terpenes. Further, they should also be capable of polymerisation with one another, giving rise to terpenes containing an uneven number of carbon atoms."

This vision of Tilden's was very accurate, and has been shown to be so by Lilley, who, by heating isoprene, obtained a first product of condensation, *mesoprene*, which under the influence of strong acids becomes converted into caoutchouc.

In 1881, moreover, Hoffmann[3] had effected the polymerisation of an isomeride of isoprene, *piperylene*, to which he attributed the constitution

$$CH_2 : CH \cdot CH_2 \cdot CH : CH_2,$$

but which, according to Thiele, is really α-methyldivinyl,

$$CH_3 \cdot CH : CH \cdot CH : CH_2,$$

an isomeride of isoprene which has a tendency to polymerise on distillation.

In 1882 Schotten[4] had obtained the same polymerisation products from the same hydrocarbon. If the investigation had been rigorously pursued, the problem of the synthesis of caoutchouc would have had its solution advanced by some years ; but the contempt in which all synthetic resinous products were held at this date caused Schotten to pass on without giving any further attention to his discovery.

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[1] *Chem. News*, 1882, 44, 170.

[2] *Trans. Chem. Soc.*, 1888, 45, 411.

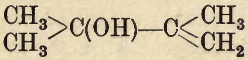
[3] *Ber.*, 1881, 14, 665.

[4] *Ber.*, 1882, 15, 425.

In 1892 Tilden, resuming his work of a decade, made an exceedingly interesting communication on caoutchouc to the Philosophical Society of Birmingham. In this he drew attention to the autopolymerisation of isoprene under the influence of time and, probably, of light; when treated with alcohol it yielded a gum which, in course of time, hardened, and a terpene, which proved to be a dipentene.

Wallach, in 1887,[1] had already found that, when kept in sealed tubes, isoprene polymerises under the influence of light to a substance resembling caoutchouc in its properties.

In 1890, Marintza [2] had also observed the production of an oily polymeride when dimethylisopropenyl carbinol,



$$\begin{matrix}CH_3\\CH_3\end{matrix}>C(OH)—C<\begin{matrix}CH_3\\CH_2\end{matrix}$$

is acted upon by dilute acids; he supposed that he was dealing with an intermediate product of the polymerisation of di-isopropenyl, but Harries was to find later that caoutchouc can also exist in an oily form.

In 1892, Couturier,[3] prior to Kondakow, showed that di-isopropenyl,

$$CH_2 : C(CH_3) \cdot C(CH_3) : CH_2,$$

polymerises very readily under the influence of heat; although he did not very thoroughly examine the gum produced, and did not make an elementary analysis of it, he nevertheless established, not only that it had the property of agglomerating into masses, but that it was soluble in ether, chloroform, and acetic acid, properties which are common to it with caoutchouc.

However interesting these various observations may have been, Tilden's communication [4] at Birmingham was of a still more definite order. Speaking of samples of isoprene which he had prepared several years previously, he said:—"I was very much surprised, a few weeks ago, to find that the contents of the flasks containing isoprene, prepared from turpentine, had entirely altered in appearance. Instead of a colourless, limpid liquid, there was now a thick syrup, in which floated several pieces of a yellow solid material. On examining it closely this was found to be caoutchouc.

"This artificial rubber, like the natural product, seems to be composed of two substances, of which one is more soluble than the other in benzene and carbon disulphide.

"A solution of synthetic rubber leaves, on evaporation, a residue which completely resembles in all its characteristics a like preparation made with Para rubber.

"Artificial rubber combines with sulphur in the same way as natural rubber, giving an elastic resistant mass."

This was the first occasion on which the possibility of vulcanising a synthetic product had been demonstrated, together with the feasibility of substituting it for the natural product, if it could only be produced at a suitable price. Tilden attributed the reaction partly to the influence of the acetic and formic acids which might have been formed by oxidation of the isoprene.

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[1] *Annalen*, 1887, 238, 88.

[2] *J. C. S.*, 1890, 58, 825.

[3] *Ann. Chim.*, 1892, 26, 485.

[4] *Chem. News*, 1892, 65, 265.

Lastly, in 1908, Tilden exhibited before the meeting of the British Association in York samples of rubber which had been formed by the spontaneous polymerisation of isoprene.

In the same year, in an interview with *The India Rubber Journal* on the subject of the synthesis of rubber, Tilden summarised the position of the problem at that time, and he did this with a freedom which deserves every respect, whatever Klages may have said.

He said :—" The transformation of isoprene may take place under one of two conditions :—

" (1) If the isoprene is brought into contact with strong hydrochloric acid, or moist hydrogen chloride gas.

" (2) By spontaneous polymerisation.

" In the former case, little rubber is formed, the product consisting mainly of the hydrochlorides of isoprene. This is, moreover, what Bouchardat pointed out in his first investigations. In the second case the change takes years to come about.

" The action of other agents, more or less powerful, such as nitrosyl chloride, only gives viscous colophene.

" If isoprene can be produced cheaply," Tilden concluded, " the hydrochloric acid process is the only one which is practicable."

Tilden's experiments were contested by Harries, who declared that, in spite of numerous attempts, he had never been able to repeat them, and above all by Klages, who, in a lecture at Dantzig, formally questioned whether Tilden had ever really obtained rubber.

Harries, although declaring that he had not been able to obtain the results described by Tilden, did not question the good faith of the English chemist, but he thought that there must be some special trick, which had not been mentioned in the descriptive memoirs on the synthesis, to enable the desired result to be obtained. Nevertheless, he mentions that Pickles,[1] in 1910, using isoprene prepared by Harries' methods, was able, at the end of three years, to obtain small quantities of rubber, formed by autopolymerisation, as indicated by Tilden.

The crude suspicions of Klages were, therefore, entirely unjustified.

Weber, in 1894,[2] in a communication to the Philosophical Society of Birmingham, fully confirmed the results obtained by Tilden, whose authority as a chemist of repute should have made Klages a little more cautious in his criticism. In a first experiment, from 100 grms. of isoprene, Weber obtained 24 grms. of caoutchouc, in the form of a white spongy mass ; in another experiment he obtained 211 grms. from 300 grms. of isoprene, and, as a by-product, 82 grms. of an oil, boiling at 245° C., and containing about 20 per cent. of dipentene. At this moment Weber had in his possession a larger quantity of synthetic rubber than any other chemist in the world. He had about 200 grms., and with this he carried out a very small number of experiments, with a view to establishing its identity with natural rubber.

Mokiewsky,[3] working in Favorsky's laboratory, found that highly purified isoprene, obtained from the dibromide, polymerised very readily.

Side by side with the polymerisation of isoprene, established by Bouchardat, Tilden, Wallach, Couturier, Weber, and Mokiewsky, other workers

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[1] *Trans. Chem. Soc.*, 1910, 97, 1085.
[2] *J. Soc. Chem. Ind.*, 1894, 13, 11.
[3] *J. Russ. Soc.*, 1898, 30, 895.

observed that most of the homologues of isoprene have a tendency to polymerise yielding ill-defined amorphous substances; as, for example, hexadiene, cyclohexadiene, cyclopentadiene, and styrolene. The polymerisation may be brought about by means of a great variety of reagents—alkalies, salts, acids—or it may occur spontaneously. These reactions were, however, noted rather than investigated; they were of a complex order, and the products were not examined very closely, but it is probable that they were composed of various polymerides of the original hydrocarbons, as must be the case with the natural products.

They should contain the three caoutchoucs which Harries has succeeded in isolating from natural rubber—viz., the oily product, the product soluble in ether, and the product insoluble in ether. Seeing what a long time is necessary to effect such separations as this, one can understand why the investigators should have hesitated to undertake such a piece of work, especially when it is remembered that they had only very small quantities of material at their disposal.

These investigations were to be continued later, after Thiele's work on piperylene[1]; Harries[2] then observed that dihydrotoluene, Klages[3] that phenylbutadiene, Kronstein[4] that cyclopentadiene, Willstätter[5] that bromobutadiene and cyclopentadiene, underwent polymerisation, yielding products resembling caoutchouc. Like isoprene and its homologues, higher and lower, all these compounds susceptible of polymerisation were characterised by the presence of two conjugated double linkings—

$$\cdot C : C \cdot C : C \cdot$$

This fact enabled Kondakow immediately afterwards to establish his theory of polymerisation, and Lebedew to formulate the following rule:—

"In hydrocarbons containing a conjugated double linking the velocity of polymerisation is greatest when the atoms 1 : 4 of the conjugated system are more heavily, and the intermediate atoms less heavily loaded."

According to this rule, dimethylbutadiene should polymerise more rapidly than either isoprene or divinyl, and this has been verified experimentally.

Kondakow, whose numerous pieces of work we have already mentioned, from the standpoint of the preparation of the different raw materials for the synthesis of caoutchouc, investigated with equal persistence and vigour all the phenomena bearing upon their condensation and their conversion into rubber. If, on the one hand, the German chemists, with a little too much of partisanship in their attitude, have ignored the work of the Russian chemist published by the *Annales de l'Université de Jurjew*, the knowledge of which had not become very common before the *Revue de Chimie pure et appliquée* published an account of it in 1912,[6] on the other hand Kondakow, despite his very real merit, committed the error of claiming priority for discoveries which were not his, and in this way, by excessive ambition, somewhat diminished the value of his own work.

Kondakow was the first to bring about the polymerisation of a homologue of isoprene, to a mass similar to rubber, which he did, in 1900,[7] by the action of alcoholic potash on dimethyl-2-3-butadiene 1·3.

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[1] *Annalen*, 1901, 319, 226.

[2] *Ber.*, 1901, 34, 303.

[3] *Ber.*, 1902, 35, 2650.

[4] *Ber.*, 1902, 35, 4151.

[5] *Ber.*, 1905, 38, 975.

[6] *Loc. cit.*, 1912; August, October, 1912; January, 1913.

[7] *J. für prakt. Chem.*, 1901, 64, 109.

In 1901, he showed that the same substance would polymerise spontaneously.

“I have recently observed,” he says, “a case of spontaneous polymerisation of this hydrocarbon (dimethylbutadiene). In February, 1900, I sealed off two 50 c.c. tubes, each containing 20 grms. of di-isopropenyl. The substance in one of the tubes had been heated with alcoholic potash at 130° C., and boiled at 69° to 69·5° C., at 754 mm. of mercury. That in the other tube, prepared from pinacone, distilled, over sodium, at 69·5° to 70° C.

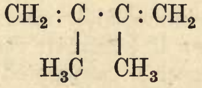
“The two tubes were allowed to stand, in the diffused light of the laboratory, until February, 1901, when I found that they contained a white spongy mass, completely filling the tubes. Neither increase nor reduction of pressure was observed on opening the tubes, and no trace of the original hydrocarbon was found in them.

“It had been converted into an amorphous, tasteless, and odourless product, elastic like rubber, and giving the same impression when pressed between the teeth.

“It appears to undergo no change in the air, is insoluble in benzene, light petroleum, chloroform, carbon disulphide, acetone, ether, alcohol, and turpentine. In benzene it simply swells up.

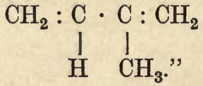
“Its behaviour towards solvents thus differentiates it from caoutchouc, and also from the polymeride previously described (isoprene polymerised by means of alcoholic potash).

“This compound interacts with bromine and hydrogen bromide is eliminated. The constitution of di-isopropenyl being represented by the formula—



$$\begin{array}{ccc} CH_2:C & \cdot & C:CH_2 \\ | & & | \\ H_3C & & CH_3 \end{array}$$

it is the simplest homologue of isoprene[1] which has the formula—



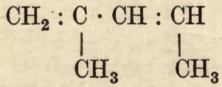
$$\begin{array}{ccc} CH_2:C & \cdot & C:CH_2 \\ | & & | \\ H & & CH_3.\text{”} \end{array}$$

The case of polymerisation described by Kondakow is, therefore, extremely interesting from the point of view of attempts to synthesise caoutchouc.

The *Gummi Zeitung* said :—“The compound formed is a perfectly amorphous substance, tasteless and odourless, and elastic like rubber. In it we have a product which must be regarded, from the chemical point of view, as the first and the most important homologue of natural caoutchouc. It is a concrete example of the possibility, hitherto unforeseen, of arriving at the synthetic production of caoutchouc,” and the note was signed by Weber.

The English chemist, returning to the subject, saw in it a possible application of the phenomena of polymerisation.

“To return,” he said, “to the subject of the polymerisation of Kondakow’s methylisoprene, Harries has already described[2] a methylisoprene having the structure



$$\begin{array}{ccc} CH_2:C & \cdot CH: & CH \\ | & & | \\ CH_3 & & CH_3 \end{array}$$

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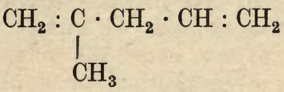
[1] *Moniteur Scient.*, 1902, 16, 323.

[2] *Ber.*, 1901, 34, 301.

which is very similar to Lioubarsky's hydrocarbon,

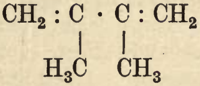


$$\mathrm{CH_2 : \underset{\overset{|}{CH_3}}{C} \cdot CH_2 \cdot CH : CH_2}$$

" One does not know whether these undergo polymerisation, but they differ widely from Kondakow's methylisoprene in that, like isoprene itself, the latter is a methylated butadiene, whereas the hydrocarbons of Harries and of Lioubarsky are pentadienes.

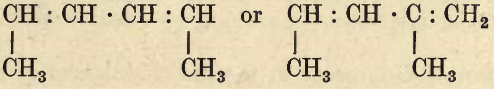
" This is why it seems to me highly probable that the latter are not able to give polymerisation products similar to caoutchouc; or, in other words, I am of the opinion that only substituted butadienes are capable of yielding rubber.

" Kondakow's methylisoprene has the structure



$$\mathrm{CH_2 : \underset{\overset{|}{H_3C}}{C} \cdot \underset{\overset{|}{CH_3}}{C} : CH_2}$$

" An extremely interesting question arises—viz., as to whether the other known isomerides, such as :—



$$\mathrm{\underset{\overset{|}{CH_3}}{CH} : CH \cdot CH : \underset{\overset{|}{CH_3}}{CH} \quad or \quad \underset{\overset{|}{CH_3}}{CH} : CH \cdot \underset{\overset{|}{CH_3}}{C} : CH_2}$$

can polymerise and yield compounds analogous with rubber.

" If, as seems to me very probable, these isomerides do not polymerise, that fact would provide a clue to the elucidation of the constitution of caoutchouc."

We may remark that, of the two isomerides in question, the first is a hexadiene, and the second a methylpentadiene.

About this time Kondakow, basing his argument upon his experimental results, as well as upon theoretical considerations, put forward a complete theory of the polymerisation of butadienes, and of the synthesis of caoutchouc, with which little fault can be found even to-day.

The theoretical considerations were based upon the analysis of a certain number of typical cases of polymerisation of unsaturated compounds, containing a double bond, and belonging to either the fatty or the aromatic series, as, for example, vinyl bromide; acrylic, metacrylic, crotonic, methylcrotonic, and methylmalonic acids; styrolene and trimethylvinylbenzene; cinnamic and atropic acids; indene, cyclopentadiene, etc.

In these examples Kondakow saw confirmation of the idea that the faculty of polymerisation possessed by these compounds is dependent upon the electro-negative groups present in their molecules. In particular, he attributed the tendency to polymerise shown by the compounds of the divinyl series to the presence in the ethenoid hydrocarbons of a new unsaturated residue, having electro-negative properties.

" The essential cause of the faculty, observed to exist amongst hydrocarbons of the divinyl series, of undergoing polymerisation, is," he wrote, " dependent in large measure, if not exclusively, upon the electro-negative properties of the molecules of these unsaturated hydrocarbons; and in the second place upon the conditions of polymerisation. All the facts brought forward, chosen from the most typical cases, completely confirm the proposition enunciated, to the effect that ethylene derivatives formed by the substitution of electro-negative elements or groups for hydrogen atoms are particularly liable to polymerise, under the influence of light (photo-polymerisation), of heat (pyro-polymerisation), or of alkalies and acids (chemical or catalytic polymerisation), or spontaneously (auto-polymerisation)."

On the basis of these propositions, Kondakow drew the deduction that the polymerisation of all divinyl hydrocarbons, known or unknown, might be anticipated, an assumption which the researches of numerous chemists showed, later on, to be quite accurate.

All syntheses actually accomplished, with the exception of that based upon the use of sodium as discovered by Matthews, seem to have been predicted, so far as the process of polymerisation is concerned, by Kondakow, in 1900-1902, and his publicaton in the *Annales de l'Université de Jurgew* seems to constitute an anticipation, not open to serious discussion, of the many patents taken out by the Bayer or the Badische Works.

Discussing isoprene and polymerisation, Kondakow put forward, again, other observations of great interest. According to him, crude, unpurified isoprene is a mixture of C_5H_8 and amylene. Since it can be condensed into rubber, amylene must play a part in the reaction, and he concludes " that a transient stage in the polymerisation of these hydrocarbons consists of dimeric, open-chain isoprenes, containing several double bonds, in the molecule."

The production of di-isoprene in the dry distillation of rubber, the preparation of myrcene, the production of secondary products in the polymerisation of butadiene and its homologues, observed by Harries and by Lebedew, are facts which tend to confirm this view.

The product obtained by Kondakow, in the auto-polymerisation of dimethylbutadiene, is, as we have seen, insoluble in most of the ordinary solvents of rubber. The Bayer Company maintained, taking their stand upon Kondakow's own declaration, and defending their patents against this anticipation, that Kondakow *had not thus* arrived at caoutchouc.[1]

Such a contention has little justification, for we know to-day that old rubber, which has been exposed for a long time to the action of light, is perfectly insoluble when brought into contact with the various reagents in which Kondakow's synthetic product is insoluble. This product must be regarded simply as resulting from a more advanced stage of polymerisation than that of ordinary synthetic rubber.

Lebedew,[2] taking up Kondakow's investigations on the polymerisation of the various hydrocarbons of the divinyl series, in Favorsky's laboratory, found that :—

(1) On heating dimethylbutadiene at 100° C. and 150° C., he obtained at 100° C. much caoutchouc and a little dimeric hydrocarbon ; at 150° C. little caoutchouc and much dimeride.

(2) By polymerisation under the influence of light, either in the cold or by heating at 50° C., for three months, the whole of the isoprene was converted into caoutchouc, and no dimeride was formed.

The synthetic rubber prepared from methylisoprene was subjected by Kondakow to dry distillation from an oil bath ; he found that under the

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[1] We shall cite the argument of the Bayer patent later.

[2] *J. Russ. Soc.*, 1909, 41, 1818.

influence of heat depolymerisation occurred, and that on fractional distillation the greater part of the liquid passed over between 220° and 360° C., leaving a residue boiling above 360° C.

All the fractions were readily soluble in ether, and all except the first—80° to 200° C.—were yellow and had a characteristic empyreumatic odour. The main fraction and the residue above 360° C. were rather viscous in consistency. The portion boiling between 80° and 100° C. has the odour of methylisoprene; on standing exposed to light it thickens and deposits rubber on the walls of the vessel; the residue smells strongly of tetramethylene.

The portion boiling between 200° and 220° C. is a dimeric olefine or terpene, which has been examined and isolated by Lebedew and Harries.

The portion passing over between 220° and 360° C. corresponds apparently with a trimeride of methylisoprene, or to the heveene obtained from Para rubber. On standing for a long time in the light it thickens and deposits colourless feathery crystals, which are probably those of oxidation products. The last portion leaves, when steam distilled, a yellow, elastic residue.

Kondakow also found that when dimethylbutadiene is polymerised—whether in presence of alcoholic potash or spontaneously—in addition to the caoutchouc polymeride there is also formed a dimeric and even a trimeric hydrocarbon. There is nothing surprising in this, for everyone who has studied the condensation of butadiene and its homologues has found that terpenes derived from the same fundamental hydrocarbon but in a lower state of condensation, are always formed in addition to the polyprene.

Harries[1] and Lebedew[2] obtained, on polymerising methylisoprene by heat, the terpenes of which Kondakow speaks: Richard[3] also obtained the dimeride on decomposing at 150° C. the synthetic product derived from dimethylbutadiene.

Kondakow[4] explains the formation of these compounds in the following way:—Under the influence of light methylisoprene is converted, first into a viscous mass which is a solution of caoutchouc in a mixture of dimolecular and monomolecular olefines as assumed by Lebedew, and not the dimolecular compound solely as maintained by Richard. This viscous mixture, formed under the influence of light, is transformed completely into a homologous caoutchouc in the dark.

This spontaneous conversion of a terpene into rubber is not surprising; if the viscous mass contained a dimeric terpene, this should normally remain unchanged in the dark. Kondakow explains this reaction by saying that the substance which was regarded as a dimeride was in reality a solution of polymerides in methylisoprene itself, which is gradually converted into polymeride; or that at some intermediate stage there is formed an unstable dimeric olefine, which is readily transformed in the process of separation into polymeride and dimeric terpene.

Richard investigated the products of decomposition, at 200° C., of the solid polymeride, and obtained results similar to those of Kondakow. From these products he separated a small quantity of methylisoprene, containing a little tetramethylene, a small quantity of trimeride and higher polymeride, and up to 50 per cent. of a dimeric terpene, the properties of which are similar

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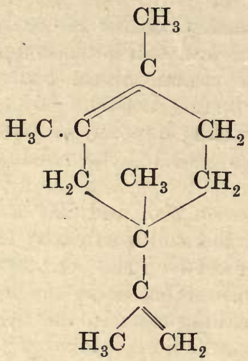
[1] *Ann. Chim.*, 1911, 383, 210.

[2] *J. Russ. Soc.*, 1909, 41, 1818.

[3] *Comptes rendus*, 1911, 153, 116.

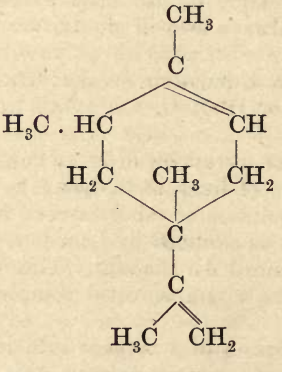
[4] *Rev. de Chim. pure et appl.*, 1912, 168.

to those of Lebedew's dimeride. According to both these authors the structure of this hydrocarbon is represented by the formula—



Its chief physical constants are as follows :—Boiling point, 85° C. at 13 mm. ; density at 20° C., 0·8598 ; molecular refraction, 54·26.

Kondakow proposes the following structural formula for the dimeric hydrocarbon formed on the destructive distillation of the synthetic rubber prepared from methylisoprene—



which only differs from the preceding formula in the position of the double bond in the nucleus. From his experiments on the polymerisation of butadiene derivatives, Kondakow drew a rather interesting conclusion, which has been already alluded to, and which is worthy of further mention.

It is well known that Harries and Klages both claim that they have never been able to repeat Bouchardat's and Tilden's experiments, in which isoprene was converted into caoutchouc by the action of halogen acids, of nitrosyl chloride, and of phosphorus pentachloride. With freshly prepared isoprene Kondakow also obtained a negative result ; but not so with isoprene which had been exposed to light for some time, for in this case the polymerisation was readily brought about by the action of halogen acids. Kondakow explains that the polymerisation must be brought about not by the influence of the acid, but rather by light action, and that the polymeride remains dissolved in the excess of the original hydrocarbon, from which it is freed and precipitated when the latter combines with the halogen acid. If this hypothesis be correct, the same result should be obtained by the addition of alcohol or acetone to the solarised isoprene.

Kondakow seems to attach very great importance to light action; he maintains that by the photopolymerisation of pure isoprene he obtained a crystalline polymeride, the methylbutadiene being completely transformed, and the action taking place in a sealed tube in the total absence of any oxidising agent.

No other worker, to our knowledge, appears to have prepared the crystalline polyisoprene described by Kondakow, which in any case would not be a caoutchouc in the industrial sense of the word, since it would possess none of the physical characteristics of rubber.

Harries,[1] Tschirch, and Chercheffsky,[2] have indeed obtained gutta and bala-gutta in crystalline form, and Willstätter [3] has also obtained a crystalline dimeride of octadiene by the distillation of dimethylammonium-methylgranatanine, but no crystalline caoutchouc, which only Kondakow has handled.

But in whatever form, it is certain that light action plays a great part in the condensation of butadiene and its homologues.

Lebedew found[4] that, in the case of isoprene, at 150° C., only 17 per cent. of caoutchouc was formed, the remainder of the hydrocarbon being converted into dimeride, whereas under the influence of light no dimeride was produced, the whole of the isoprene yielding caoutchouc. Ostromisslensky [5] and Koch [6] obtained a similar, but much more rapid, condensation with ultra-violet radiation, and the result is similar when the electric current acts upon divinyl derivatives.

Collie [7] had already drawn attention to a similar action. "Under the influence of the silent electric discharge," he said, "ethylene combines with carbonic oxide at ordinary temperatures, and then polymerises, yielding $C_{10}H_{20}$ hydrocarbons. If the polymerisation be forced a substance similar to caoutchouc, and having the composition $(C_5H_8)_x$, is formed."

According to Kondakow, isoprene polymerises a hundred times more slowly than methylisoprene, and butadiene still more slowly than isoprene; it is upon these observations that Lebedew's rule, referred to above, is based.

The work just described, beginning with Bouchardat and continued up to Kondakow's researches, only constitutes, so to speak, the preface to investigations on the synthesis of caoutchouc which have undergone enormous development, more particularly within the last five years. The formidable consumption of rubber brought about by the use of motor vehicles, together with the attempts made in Brazil at the valorisation of the raw material—which it is true have not been very successful—have stimulated investigators to unwonted activity, and have led to an *almost industrial* solution of the problem before them. In fact, it is to-day a question rather of coming to the point than of the working out of a principle.

Perkin very truly says:—"The situation in 1906 might be summed up in this way: it had been recognised, in a more or less general way, that most compounds containing a system of conjugated double linkings, show a tendency to polymerise, more or less readily. The polymerides are either viscous,

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[1] *Ber.*, 1903, 36, 1935.

[2] *Brit. Ph.*, 1905, 243, 358.

[3] *Ber.*, 1905, 38, 1975-1980.

[4] *J. Russ. Soc.*, 1909, 41, 1868.

[5] *J. Mendeleef*, Dec. 28, 1713.

[6] *Chem. Zeit.*, 1912, 36.

[7] *Trans. Chem. Soc.*, 1905, 87, 1540.

ill-defined substances, or well-characterised caoutchoucs; or, again, hard resinous solids, like polystyrolene. Their properties vary according to their method of preparation, and according to the molecular weight of the hydrocarbon employed as raw material. The methods of polymerisation of the selected substance may be reduced to the action of heat, of light, of chemical reagents, acid or alkaline, and spontaneous polymerisation."

In the majority of cases the methods employed were not very efficient as regards yield, and were very slow; further discovery became necessary.

The sudden increase in the price of rubber to 12s. per lb., as a result of the operations of the Belem "Valorisation" Committee, gave a great impetus to all investigations, and it is from this time that the great progress made, both in the preparation of raw materials and in their polymerisation, dates.

Heinemann, regardless of the vigorous and somewhat unjustifiable criticism of Harries, seems to have been the first to work on practical lines. We have described the manner in which he prepared isoprene, adopting an old idea of Berthelot's, and condensing acetylene, ethylene, and methyl chloride under the influence of heat.

In his English Patent 21,772 of 1907, and his German Patent 44,828, of October, 1908, both prior to the Bayer Patents of September 11th, 1909, he described the polymerisation of isoprene as follows:—"This hydrocarbon, isoprene, contains two double bonds, and consequently polymerises readily. This may be brought about, as is known, by heating in a sealed tube with or without the addition of acid, alkali, or neutral catalysts. The temperature is preferably kept at 100° to 150° C. for three days; higher temperatures hasten polymerisation, lower temperatures retard it. After polymerisation a mass resembling rubber, but dissolved in the excess of the original hydrocarbon, or in an oily polymeride, is obtained. The hydrocarbon solvent can be separated by distillation, or the caoutchouc formed may be precipitated by the ordinary means, such as the addition of alcohol or acetone."

In a later patent[1] Heinemann employed another method of operation. Making use of an observation by Greville Williams which we have already mentioned, he passed oxygen for six hours into a cooled solution of 1 litre of isoprene in turpentine, about 20 litres of the gas being used.

The product was then heated in a closed vessel, from 40° to 105° C., for a length of time sufficient to thicken the mass; this varied from a few hours to a few days, according to circumstances. The caoutchouc formed was then separated, either by distilling the volatile constituents in steam, or by precipitation with alcohol and acetone.

The oxygen employed could be obtained either by the electrolytic decomposition of water, or from hydrogen peroxide, or by the action of sulphuric acid on barium dioxide. Ozone also gave very good results.

In 1909, a sample of this rubber of Heinemann's was sent by Hempel, of Dresden, to Harries for identification. Harries established the fact that the product in question was a true caoutchouc, yielding levulinic aldehyde when its ozonide was decomposed with water, and forming a nitrosite with nitrous acid, but, in view of the fact that the sample submitted resembled Para in external appearance, he replied to the effect that the product was

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[1] Eng. Pat. 14,041, June 10, 1910; Ger. Pat. 54,443, June 6, 1911.

certainly caoutchouc, but that at the same time he advised the sender to make sure, before interesting himself further, that it had been produced in Dr. Heinemann's experiments.

He says again :—" I had to repeat Heinemann's experiments. I know that that has already been done by others, but neither I nor they have been able to confirm in any way the data of the English patent.

" If isoprene should really be produced by the reaction, and, from the isoprene, caoutchouc, such special conditions appear to be necessary that they ought to have been pointed out, with all necessary explanations, in the patent specification."

The failure of Harries to repeat the syntheses of Heinemann and of Tilden is not easy to explain. The first stage, relating to the production of butadiene is classic, and Berthelot's experiment in which ethylene and acetylene were condensed in a red-hot tube can be verified any day, although the yields are not excellent.

There is nothing impossible about the methylation of butadiene, and the polymerisation of the product to caoutchouc by oxidation—a fact already noted by Greville Williams—and by heating at moderate temperatures is by no means improbable.

It is not easy to understand why Harries, with his great experimental skill, should have been unable to repeat such a simple synthesis, and should have denied the possibility of realising it.

The work of Harries on the analysis, as well as on the synthesis of caoutchouc, is of such great importance that it is regrettable to see him making use of the authority which he has rightly acquired to deny any value to synthetic processes discovered elsewhere than in Germany.

Simultaneously with the discovery, by Hoffmann and Coutelle, of the Elberfeld Farbenfabriken, of a method of polymerising isoprene and its homologues to products which Harries recognised to be similar to rubber, and of which we shall shortly speak, the latter author also worked out a process of polymerising divinyl derivatives. Describing his discovery in a lecture before the Society of Engineers at Vienna, on March 12th, 1910, he said :—

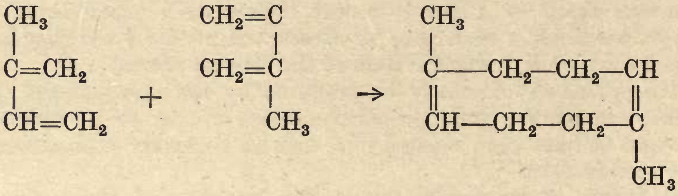
" I have shown you that insoluble caoutchouc can be transformed into soluble caoutchouc by heating it in presence of acetic acid. It was this fact which suggested to me the idea that there might be a state of equilibrium in which, on the one hand, caoutchouc could undergo still further polymerisation under the influence of acetic acid, and on the other hand could be reconverted into caoutchouc by a directly reversible reaction.

" Starting from this ground, I heated isoprene with acetic acid, and on account of the volatility of the liquid, carried out the operation in a sealed tube.

" I noticed then that at a temperature a little above 110° C., a product separated out, having all the properties of caoutchouc. Pure synthetic isoprene showed itself to be more readily polymerised than isoprene obtained from rubber. Later, I discovered still other methods, but I found that if the conditions of experiment are not rigidly adhered to, all kinds of thick, sticky oils, resins, and lacs are obtained, but no caoutchouc."

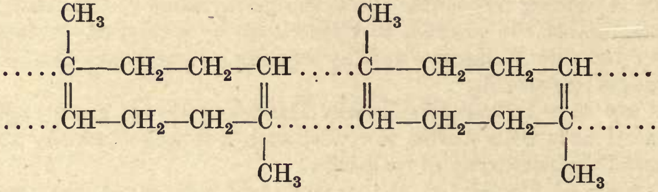
Artificial rubber is quite as tough and elastic as natural rubber, and as obtained varies in colour from light brown to pure white.

On attempting to form an idea of the mechanism of the change, the conclusion is reached that the isoprene is first of all converted into dimethylcyclo-octadiene—

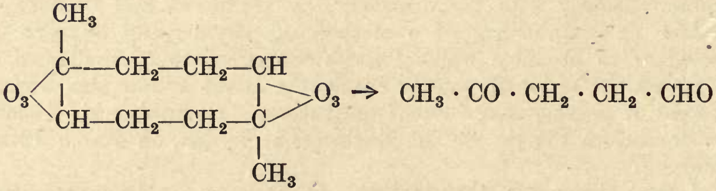


Isoprene. Isoprene. Dimethylcyclo-octadiene.

and that then x molecules of dimethylcyclo-octadiene condense with one another, for example, according to the following scheme :—



The formation of levulinic aldehyde by hydrolysis of the ozonide is proof that the condensation can only take place in this manner.



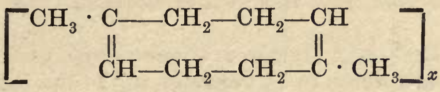
$CH_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CHO$

There follows, from this experiment, the possibility of converting most of the hydrocarbons containing conjugated double linkings into substances allied to caoutchouc, as stated by Kondakow in 1903.

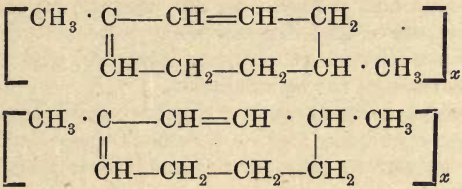
Harries' acetic acid process is applicable to all derivatives of butadiene, and we give below some information explanatory of the process and control of the methods employed in practice. It is probable that, as suggested by Harries, the acetic acid plays the part of solvent and not of coagulant towards isoprene, and that the principal condensing agent is heat. Yet, if one recalls the part played by acetic acid in the coagulation of latex, and if one compares the electrolytic theory of condensation put forward by Kondakow with the electrolytic theory of coagulation put forward by Victor Henri, it seems probable that acetic acid must act both as a condensing agent and as a solvent. Under these circumstances formic acid should have a still more powerful action, and its use should permit of the employment of lower temperatures ; the difficulty which was at first experienced in its use—viz., the production of resins—must be due to the employment of too high a temperature. In polymerisation, whether spontaneous, or brought about by heat or in presence of solvents such as acetic acid, small quantities of substances other than caoutchouc—properly so-called—are always formed. These yield ozonides, which on hydrolysis split up into other products than levulinic aldehyde.

One of these behaves like pyruvic aldehyde, or methylglyoxal, which would indicate the presence in the polymerised substance of an isomeride in which the double bonds are in different positions from those of the normal compound.

For example :—



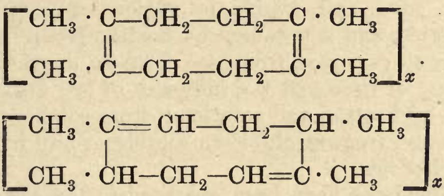
Normal caoutchouc.



Abnormal caoutchoucs.

In the case of dimethylbutadiene this formation of isomerides is still more definite. By the action of ozone on the caoutchouc produced two ozonides are obtained, of which one gives on hydrolysis acetonylacetone, and the other products which are powerful reducing agents, and belong to the keto-aldehyde family.

Hence two differently constituted caoutchoucs are present, to which the following formulæ may be given :—



The surest method, according to Harries, of characterising these different bodies, consists in preparing their ozonides and decomposing them, because in this way simpler compounds are obtained, which frequently form phenylhydrazones or similar well-crystallised derivatives.

Harries investigated the application of his process of polymerisation by means of acetic acid, successively to isoprene, butadiene, and dimethylbutadiene. He described as *normal caoutchoucs* those which are formed on the polymerisation by heat, either alone, or in the presence of acetic acid, of divinyl and its derivatives, and as *abnormal caoutchoucs* the secondary products which are formed in small quantity in the course of the reaction, and accompany the *normal caoutchoucs*.

Abnormal caoutchoucs are also obtained by polymerising the same hydrocarbons by means of sodium, as we shall see later.

In order to avoid confusion, we shall always refer to these last-named rubbers as *sodium caoutchoucs*.

We shall now describe the successive results obtained by Harries.

Equal volumes of isoprene and glacial acetic acid are heated together for eight days, in a sealed tube, in a water-bath at 100° C. The oil which separates from the colourless solution is decanted and washed with alcohol. It is then placed in a vacuum desiccator, where, after a longer or shorter interval, it solidifies to a plastic product. The yield varies from one experiment to another, and Harries has not discovered the reason for this variation.

The result described by Harries is obtained with variations in the amount of acetic acid from 2 drops to 1½ volumes, and in the temperature from 100° to 120° C. The liquid remains strongly acid for weeks, even when the smallest proportion of acetic acid is used. In this case the oil containing the caoutchouc does not separate, and it is necessary to remove first of all the excess of isoprene, by distillation at ordinary pressure, and then the dimerides formed as by-products of the condensation.

The thick residue is dissolved in ether, and precipitated by alcohol, when a white substance is obtained, which becomes transparent on drying, and has properties very similar to those of natural rubber which has been precipitated from solution.

If the temperature has been taken up to 110° C., the product is of a brownish colour.

When freshly prepared, synthetic rubber is soluble in ether, benzene, and chloroform; in course of time, however, it becomes difficultly soluble and even insoluble, in which case it simply swells up and forms a gelatinous mass with the solvent. On referring to earlier work of Harries, which we have summarised, on the subject of natural caoutchouc, it will be seen that the purified rubber can exist in three forms; the first is an oily modification, produced by the action of heat on $C_{10}H_{16}$ in solution; the second is ordinary rubber, solid, and soluble in various solvents; and the third is completely insoluble, and is obtained by heating freshly precipitated rubber.

The polyterpene can pass from one form to another; from the oily to the solid, by lapse of time and the influence of low temperatures; from the solid to the oily by heating and solution; from soluble to insoluble by lapse of time; and lastly, from insoluble to soluble or oily by heating with acetic acid or acetic anhydride.

Similar modifications have been observed in the case of synthetic caoutchouc, which becomes insoluble the more readily as it is the more highly purified.

The process worked out by Harries gives better results, from the point of view of yield and of quality, with pure, synthetic isoprene than with isoprene obtained by destructive distillation of rubber. A similar observation had already been made by Kondakow. The product obtained when isoprene from rubber is employed is often oily or viscous in character.

The caoutchouc obtained by Harries' method must be kept, when dry, in an atmosphere of carbon dioxide, and protected from light, since, like highly purified natural rubber, it is attacked by the oxygen of the air, becoming brittle, and losing all its rubbery properties.

As Kondakow found, the yield varies according to whether the polymerisation has been carried out at 95° C. or above 100° C.; in the latter case the proportion of dimerides formed is smaller. It follows that the lower the temperature at which one can carry out the process, the better will be the yield of synthetic product. The synthetic caoutchoucs obtained at temperatures above 100° C. are much less stable than those obtained at 95° C.

On elementary analysis the synthetic product obtained from isoprene by the method of Harries gave the following results :—C = 86·92, H = 11·87 per cent. $C_{10}H_{16}$ requires C = 88·2, H = 11·7 per cent.

These figures are similar to those given by caoutchouc which has been purified by a single precipitation.

The residue obtained from a solution prepared by heating with benzene for two days on the water-bath gives on analysis the following figures :—C = 82·93, H = 11·15 per cent. $C_{10}H_{16}$ requires C = 88·2, H = 11·7 per cent.

This substance must be an oxidation product, although it retains the chemical properties of caoutchouc, yielding a nitrosite which decomposes at 157° to 160° C., and a tetrabromide. Isoprene rectified over sodium in an atmosphere of carbon dioxide, and polymerised by Harries' method is completely soluble in ether. Its composition as revealed by analysis is C = 88·08 to 88·04, H = 11·25 to 11·41 per cent. $C_{10}H_{16}$ requires C = 88·2, H = 11·7 per cent.

This product is, therefore, nearly pure.

It is probable that the insoluble modification is not peculiar to the synthetic product, and that it occurs under conditions identical with those in which it is formed in the natural product; nevertheless, the synthetic caoutchoucs polymerised above 100° C. oxidise much more readily than the others.

On vulcanisation, Harries' synthetic product seems to behave like that obtained by Tilden. Harries employed the cold method of vulcanisation, with sulphur chloride, almost exclusively; it was in fact the only method practicable with the small samples which he obtained.

It was noticed that the best vulcanised products were those prepared from samples which had been polymerised at the lowest temperatures. The bromination of synthetic caoutchouc was carried out for comparison with purified Para. Harries says, with respect to this :—"As soon as they came into contact with the solution of bromine, the two test samples began to give off hydrogen bromide, the synthetic sample more vigorously than the other."

When the bromide has been precipitated by alcohol, after standing for six hours, it is filtered off and washed with a mixture of 2 parts of chloroform and 1 part of alcohol. The product obtained from synthetic caoutchouc is slightly soluble in carbon disulphide; that obtained from natural rubber does not pass completely into solution. There remain highly swollen particles resembling the insoluble modification *c*, and filtration must be carried out through glass wool. If solutions of the two bromides be run, drop by drop, into alcohol or petroleum ether, the synthetic product is precipitated as a fine white powder, the other as adherent clots, which cannot be brought into the same condition by desiccation and grinding. The tetrabromide does not decompose at a definite temperature when heated; it loses its colour slowly and decomposes completely at about 140° to 150° C.

The behaviour of the two bromides at different temperatures is shown in the following table :—

Temperature.	Bromide from	
	Natural Caoutchouc.	Synthetic Caoutchouc.
125° C.	Slight colouration, . . .	Rather marked colouration.
140°	Strong ,, . . .	Very deep ,,
145°	Blackening, and decomposition.	Blackening, and evolution of HBr.

It is known that with nitrous acid natural rubber yields two products: the insoluble compound has the composition $C_{10}H_{16}N_2O_3$. On prolonged contact with the mother liquor, in presence of excess of nitrous acid, the whole of the nitrosite becomes fairly soluble in ether and in acetone, and after several precipitations from ethyl acetate, a product is obtained which Harries calls *nitrosite C*, and which has the formula $C_{10}H_{15}N_3O_7$, with a fixed decomposition point of 158° to 162° C. Synthetic caoutchouc behaves in the same way towards nitrous acid as natural rubber; its *nitrosite C* has the same composition and the same decomposition point, 158° to 162° C.

On analysis these nitrosites give :—$C = 40{\cdot}66$, $H = 5{\cdot}98$, $N = 13{\cdot}20$ per cent. $C_{10}H_{15}N_3O_7$ requires $C = 41{\cdot}52$, $H = 5{\cdot}23$, $N = 14{\cdot}54$ per cent.

The figures obtained for the synthetic product are not so close to the theoretical values as those obtained for the natural product. The decomposition points are as follows :—

Rubber.	Nitrosite A.	Nitrosite C. Precipitated three times.
Para, ...	95° C.	145°-157° C.
Synthetic—autopolymerised, .	115°-120° C.	145°-140° C.
,, —by acetic acid, .	brown at 130°-135° C.	145°-147° C.

Towards ozone[1] Harries' synthetic product behaves like natural rubber. In order to obtain the ozonide it is necessary to pass 12 per cent. ozone for about three hours into a pseudo-solution in chloroform or carbon tetrachloride. The fixation of O_3 takes place more slowly than with Para.

The solution remains clear; the oily residue, obtained on evaporation *in vacuo* on the water bath, is soluble in ethyl acetate, from which it is precipitated by petroleum ether; after purification and desiccation over sulphuric acid, it has the appearance of a thick oil, having the same characteristics as the ozonide of natural rubber. It will only solidify to a glassy solid if highly purified isoprene has been used in the preparation of the caoutchouc.

On analysis it gives :—$C = 50{\cdot}80$, $H = 6{\cdot}99$ per cent. $C_{10}H_{16}O_6$ requires $C = 51{\cdot}72$, $H = 6{\cdot}95$ per cent. It explodes violently when heated on platinum foil, dissolves at once, without decomposition, in boiling water, and then splits up like the natural product.

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[1] The formation of ozonides of caoutchouc was discovered by Wreight (*Bull. Soc. Chim.*, 1897, 18, 438) prior to Harries.

Starting with 5 grms. of caoutchouc, 7·5 grms. of diozonide are obtained. 7 grms. of diozonide yield on hydrolysis—

Levulinic acid (boiling point, 130° to 160° C. at 12 mm.),	3·2 grms.
„ aldehyde,	1·5 „
Undecomposed resin,	0·4 „
	5·1 „
Loss,	1·9 „
	7·0 „

In preparing the phenylhydrazone of levulinic acid, a crystalline phenylhydrazone, melting at 148° C., is precipitated from the alcoholic mother liquor; Harries regards this as methylglyoxalosazone, denoting the presence of the isomeride which we have already referred to. The levulinic acid obtained from synthetic caoutchoucs is much more difficult to purify than that obtained from the natural product.

On distillation *in vacuo*, synthetic caoutchouc gives the same products as natural rubber, even at 2 mm.; at 120° C. the mass melts and froths a great deal; at 180° C. oils begin to pass over which become thicker and develop colour; at 220° to 260° a thick yellow oil is obtained. Isoprene in excess passes over at the beginning of the distillation.

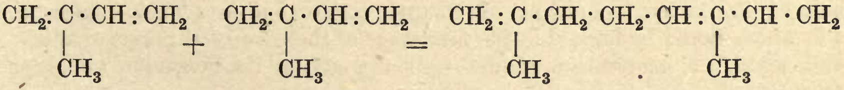
The fraction 220° to 260° C. was converted into ozonide; this did not give a trace of levulinic acid on hydrolysis. It follows that the molecule of synthetic caoutchouc is completely broken down by destructive distillation.

In polymerisation by Harries' method, as in the other processes, various secondary products are formed in addition to caoutchouc; the existence of these had already been pointed out by Bouchardat,[1] by Wallach,[2] who recognised dipentene amongst them, and by Kondakow. In addition to dipentene Harries finds another terpene which Lebedew has also recorded as present amongst the products of autopolymerisation. This substance boils at 63° to 65° C. at 12 mm., and seems to be related to myrcene. It has the following physical constants:—

$$d^{18°}_{18°} = 0{\cdot}8451, \quad n^{18°}_{D} = 1{\cdot}47408. \quad n^{18°}_{\alpha} = 1{\cdot}47113, \quad n^{18°}_{\gamma} = 1{\cdot}48860.$$

From the mass of dimerides thus formed it has only been possible to separate—by Wallach's method using bromine and acetic acid—a very little dipentene bromide. By the action of ozone an oily ozonide is obtained.

Harries regards this substance as an open-chain terpene, $C_{10}H_{16}$, formed from two molecules of isoprene in the following manner:—



$$\mathrm{CH_2:\underset{\underset{\displaystyle CH_3}{|}}{C}\cdot CH:CH_2} + \mathrm{CH_2:\underset{\underset{\displaystyle CH_3}{|}}{C}\cdot CH:CH_2} = \mathrm{CH_2:\underset{\underset{\displaystyle CH_3}{|}}{C}\cdot CH_2\cdot CH_2\cdot CH:\underset{\underset{\displaystyle CH_3}{|}}{C}\cdot CH\cdot CH_2}$$

Isoprene. Isoprene. Di-isoprene.

The same product is also obtained by heating pure isoprene at 300° C. as shown by Bouchardat. Lebedew, under almost identical conditions, but

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[1] *Bull. Soc. Chim.*, 1875, 24. 112.

[2] *Ber.*, 1902, 35, 3265.

heating only at 150° C., obtained in addition to dipentene, a dimeric hydrocarbon containing a cyclic nucleus, and having a structure very different from that of dipentene.

Lebedew has also come to the conclusion that, starting with isoprene, one can obtain four dimeric cyclic hydrocarbons, and it may be supposed that, as suggested by Harries, open-chain dimerides are also formed.

These questions of secondary polymerisation, in spite of the somewhat confused explanations attempted by Kondakow, remain very obscure. It may be supposed, and it has indeed been shown, that such changes are dependent (1) upon the purity of the isoprene employed; (2) upon the temperature at which polymerisation is effected, the lowest temperatures being the least favourable to their occurrence.

From the technical point of view the investigation of this question will have to be taken up very seriously, for the yield of caoutchouc, which is of the highest importance, depends entirely upon it.

Neither Harries nor any other investigator up to now appears to have studied the action of chromyl chloride on the synthetic products. Spence and Galletly[1] have shown that this reagent forms with caoutchouc a compound having the composition $C_{10}H_{16}(CrO_2Cl_2)_2$, which is decomposed by water yielding an aldehyde.

Harries has applied his method of polymerisation by means of acetic acid to the case of butadiene. He finds that, in order to get results a rather higher temperature—110° to 120° C.—must be employed, and maintained for 16 days. The caoutchouc thus obtained is transparent, gelatinous, and non-elastic, and dissolves with difficulty in solvents other than chloroform.

On analysis it gives $C = 87{\cdot}04$, $H = 11{\cdot}31$ per cent. C_8H_{12} requires $C = 88{\cdot}88$, $H = 11{\cdot}11$ per cent.

Unless the butadiene is carefully purified oxidation always takes place.

The butadiene rubber obtained by Harries' method is converted by ozone—in chloroform solution—into an oily, explosive ozonide, which on hydrolysis with water yields an aldehyde; the latter gives an intense pyrrol reaction, strongly reduces Fehling's solution, and gives the hydrogen peroxide reaction. It appears to be succinic dialdehyde, but Harries was unable to characterise it on account of the small quantity obtained. In carbon tetrachloride solution the same synthetic product gives a solid, white ozonide, which is only decomposed by water with difficulty. It also gives the pyrrol reaction, but the formation of hydrogen peroxide cannot be detected, even by means of titanic acid.

Lebedew had already obtained from butadiene rubbers a similar ozonide, having the formula $C_8H_{12}O_6$.

Harries carried the investigation of these ozonides further, and drew the following interesting conclusions:—

"My earliest observations had led me to regard the fundamental molecule of the lower homologue of natural caoutchouc as a cyclo-octadiene, 1·5, which would be formed in the first stage of the process of polymerisation, and which on ozonisation should split up, giving its diozonide or being regenerated.

"The diozonide of Willstätter's cyclo-octadiene is already known;[2]

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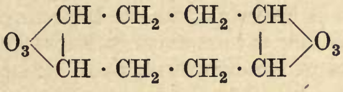
[1] *Gummi Zeit.*, 1911, 25, 1032.

[2] The cyclo-octadiene is obtained by the aid of pseudo-pelletierine (*Ber.*, 1905, 38, 1975).

it is a white powder, highly explosive, and is decomposed by water with difficulty, without giving the hydrogen peroxide reaction."

But we have just seen that the diozonide of the synthetic product from butadiene may be either an oil or a solid, according to the solvent employed in its preparation, and the solid bears the strongest resemblance to the diozonide of cyclo-octadiene.



With nitrous acid Harries' synthetic butadiene rubber gives a nitrosite soluble in ethyl acetate, from which it is precipitated as a yellow amorphous solid, which decomposes at 80° C. with frothing.

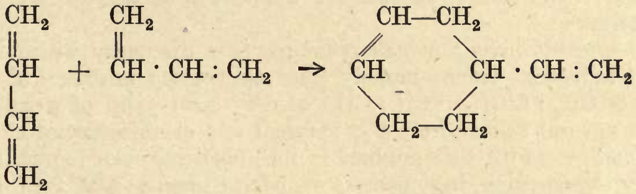
In this polymerisation there is produced, in addition to the caoutchouc, a terpene boiling at 36° C. at 13 mm., and having the following physical constants :—

$$d_{4^\circ}^{16^\circ} = 0{\cdot}8523, \quad n_D^{16^\circ} = 1{\cdot}46768, \quad n_\alpha^{16^\circ} = 1{\cdot}46423, \quad n_\gamma^{16^\circ} = 1{\cdot}48812.$$

The empirical formula of this compound is C_8H_{12}, the following figures being obtained on elementary analysis :—$C = 88{\cdot}23$, $H = 11{\cdot}0$ per cent. C_8H_{12} requires $C = 88{\cdot}88$, $H = 11{\cdot}11$ per cent.

It gives a yellow colouration with concentrated sulphuric acid, and a reddish-yellow with alcoholic sulphuric acid. In chloroform solution it gives a white, explosive ozonide, which is difficultly soluble, and is decomposed by boiling water yielding an aldehyde with a strong pyrrol reaction.

By analogy with the formation of dipentene from isoprene, Lebedew ascribes to it the following formula :—



Butadiene. Butadiene. Lebedew's terpene.

A hydrocarbon of this structure should, on hydrolysis of its diozonide, yield a derivative of succinic aldehyde.

As will be seen, Harries' process of polymerisation has given only very mediocre results in the case of butadiene ; a caoutchouc is obtained having none of the characteristic physical properties of ordinary rubber, and at the same time only sparingly soluble in the usual solvents.

The results obtained with dimethylbutadiene have been no better, for the product is still viscous and yellowish. Harries abandoned the investigation of it in order to devote the whole of his attention to caoutchoucs produced by autopolymerisation, obtained by the method of Hoffmann and Coutelle ; he, therefore, prepared neither the tetrabromide nor the nitrosite, nor yet the ozonides of this synthetic product.

In short, Harries' process—in which heat is employed in the presence of acetic acid—does not work well with isoprene, and is not of much use in the case of its homologues.

The Bayer works, under the vigorous stimulus of Duisberg, have had the preparation of synthetic caoutchouc under investigation for seven or eight years, and their chemists, Drs. Hoffmann and Coutelle,[1] were the first to realise an industrial synthesis. The application for a patent was made in Germany on September 11th, 1909.[2]

The process consists in heating synthetic isoprene with or without agents which favour polymerisation, at temperatures below 250° C. This very simple solution of the problem of condensation, upon which the patience and ingenuity of so many investigators had been exercised, recalls, as Harries says, the story of Christopher Columbus and the egg; he also declares it to be surprising.

The work of Schotten, dating from 1882; that of Hoffmann on piperylene, dating from 1881; that of Couturier, of 1892, on the polymerisation of diisopropylene by heat, had, although a prudent silence has been maintained on the subject, somewhat cleared the way for the Bayer chemists, and it was known in 1909—Couturier had shown—that the derivatives of divinyl could be polymerised under the influence of heat.

As Perkin very rightly observes, Heinemann in his English Patent 21,772 of 1907, had provided for the employment of heat under conditions identical with those claimed by the Bayer works, and perhaps with greater precision.

Hoffmann maintains that Heinemann's German application did not specify these details, which would have been added afterwards. Moreover, the German Patent Office refused a patent to Heinemann; but what Foreign Patent, however sound, does not the Patent-Amt refuse, when national interests are in question?

The first Bayer patent deals only with the polymerisation of isoprene: it provides, then, for the formation of a substance identical with natural caoutchouc. The text of the patent, which it is as well to have before us, runs as follows:—

"The present invention has reference to a discovery which is of great technical industrial value—namely, that on heating isoprene, of which the formula is $CH_2 : C(CH_3) \cdot CH : CH_2$, a very good yield of a substance resembling natural rubber from the physical and chemical point of view, and able to compete with this product in its industrial uses, is obtained. This discovery is surprising, inasmuch as Wallach (*Annalen*, 227, 295), by heating isoprene prepared from natural rubber, obtained only dipentene, whilst Bouchardat (*Bull. Soc. Chim.*, 2, 24, 112), by heating isoprene derived from the same source, obtained only a mixture consisting principally of dipentene, together with a resin resembling colophony. These divergent results may be explained by the fact that the so-called isoprene, hitherto used in polymerisation experiments, was too impure.

"The temperature may vary within wide limits, but if 100° C. be much exceeded considerable quantities of terpenes are very liable to be obtained. In carrying out the reaction, appropriate diluents or solvents, or catalytic agents of neutral, alkaline, or acid character may be added to the isoprene.

"*Example* 1.—200 parts of isoprene are heated in an autoclave at 200° C. for 10 to 12 hours. By the end of this time a very tenacious, elastic, but still

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[1] *Ann. de Chimie*, 1911, 385.

[2] Fr. Pats. 414,382, 419,316.

sticky mass is formed. It is treated with steam, and the mass then loses its viscosity and is converted into a substance resembling natural rubber.

"*Example* 2.—500 parts of isoprene are heated in an autoclave at 90° to 100° C. for six days. Steam is then introduced into the viscous mass, first of all at ordinary pressure, until all the unattacked isoprene is driven off, then at a lower pressure until no more oil distils. On cooling a pure white caoutchouc of excellent quality remains in the distillation apparatus.

"*Example* 3.—A solution of 100 parts of isoprene in 200 parts of benzene is heated in an autoclave at 120° C. for two days. The liquid is distilled, unchanged isoprene, benzene, and a terpene passing over and leaving behind a tenacious, transparent mass, which on washing with alcohol loses its transparency, and assumes the appearance of caoutchouc.

"*Summary.*—The invention comprises :—

"(1) A process for producing a substance resembling natural caoutchouc, which consists in heating isoprene with or without the addition of neutral, alkaline, or acid reagents.

"(2) The new product and its industrial use."

It was the caoutchouc obtained by this process which, in November, 1909, Duisberg submitted to Harries for analysis, and which the latter declared to be identical with natural caoutchouc, since it gave the same tetrabromide, the same nitrosite, and an ozonide which on hydrolysis yields levulinic acid and aldehyde.

After this principal patent covering the condensation of isoprene, the Bayer works took out a whole series of patents, covering the polymerisation of the analogous hydrocarbons, butadiene, and dimethylbutadiene.

German Patent 235,423, of September 30th, 1909, has for its object the polymerisation of erythrene ; the process is carried out in a manner analogous to that described for isoprene. Patent 250,335, of December 27th, 1909, accepted on January 26th, 1911, relates to the polymerisation of β-γ-dimethylbutadiene. It is in this patent that the criticism of the initial work of Kondakow on the polymerisation of methylisoprene, either by alcoholic potash or spontaneously, occurs ; Kondakow's methods, of which we have already spoken, were worked out in 1901. We think it will be of interest to reproduce this passage in the patent specification :—

"Kondakow has described products of the polymerisation of β-γ-butadiene. In the *Journal für praktische Chemie* (1900, 62, 175-176) the author mentions that on heating di-isopropenyl with alcoholic potash (1 KOH : $3C_2H_5 \cdot OH$) up to 150° C., he succeeded in polymerising a portion of the hydrocarbon and converting it into a mass resembling leather—elastic, recalling caoutchouc, or the polymerides of styrol. But the other properties of this polymerisation product, spoken of by Kondakow, show that he was not really dealing with a product analogous with rubber. Whereas natural rubber is characterised by complete insolubility in alcohol, Kondakow's product, as he expressly mentions (p. 176), was soluble in alcohol. It is probable that the author was dealing with a lower polymeride of β-γ-dimethylbutadiene.

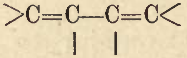
"Later on, Kondakow (*J. für prakt. Chem.*, 1901, 64, 109-110) described another polymerisation product of dimethylbutadiene, obtained by exposing dimethylbutadiene to diffused light in a sealed tube, for a period of one year. This product was as elastic as rubber, but was totally different from the polymerisation product previously described. This polymeride was insoluble in all solvents, and, therefore, cannot be regarded as a substance analogous with rubber. It is probable that this product which results from the action of light is a substance of a higher degree of polymerisation than natural rubber."

In the same patent, the Bayer works recall the fact that Couturier had already, eight years before (*Ann. de Chim.*, 1892, 26 [vi.], 489), pointed out that β-γ-dimethylbutadiene is converted into a viscous mass by the action of heat alone.

By way of supplementary detail the authors pointed out in their application that it is necessary to carry polymerisation to such a point that the resultant product is insoluble in alcohol, but soluble in benzene. The mode of procedure is practically the same as in the case of isoprene; the duration of the heating process varies from 24 hours at 150° C. to 8 days at 100° C., from 12 hours at 200° C. *in vacuo* or in an atmosphere of carbon dioxide to three months at 35° C.

The patent covers also the polymerisation of tetramethylerythrene, and the use of creosote with β-γ-methylbutadiene. In the latter case the treatment lasts five days at a temperature of 90° C.

These various patents were completed by a comprehensive patent of December 28th, 1909 (Ger. Pat. 235,686), which covers all hydrocarbons containing a conjugated double linking—



$$>C=\underset{|}{C}-\underset{|}{C}=C<$$

other than butadiene, isoprene, and methylisoprene.

Its object is the production of substances analogous to caoutchouc, starting from substances in which the free valencies are satisfied partly by hydrogen, partly by alkyl groups (erythrene, isoprene, and β-γ-dimethylbutadiene being excepted), with or without diluents or catalysts.

As examples of the method of manufacture, the following are given:—

Example 1.—100 parts of α-methylbutadiene,

$$CH_3 \cdot CH : CH \cdot CH : CH_2,$$

is heated in an autoclave at 100° C. for 24 hours; after cooling, the excess of α-methylbutadiene is distilled off, and the residue is steam-distilled. The product is a white substance isomeric with caoutchouc.

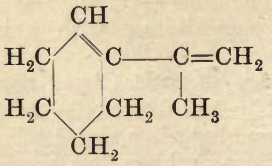
Example 2.—500 parts of α-α-dimethylbutadiene—

$$(CH_3)_2C : CH \cdot CH : CH_2$$

is heated for eight days at 90° to 100° C., or *in vacuo* for 12 hours at 200° C., and the product is steamed.

In *Example No.* 1, 5 per cent. of formic acid may be added.

Example 3.—Under the same conditions as *Example* 1, 500 parts of the erythrene derivative having the formula—



are subjected to the action of heat.

Example 4.—α-methylbutadiene is heated in an autoclave at 55° C. for three months, and the product is steam-distilled. Tetramethylerythrene—

$$(CH_3)_2C : CH \cdot CH : C(CH_3)_2$$

may also be employed.

With these other substances, as with butadiene and its homologues, creosote may also be employed as a condensing agent.

Apart from the addition of formic acid as a condensing agent, which is very similar to the employment of acetic acid for the same purpose (a process patented a month later in January, 1910) by Harries, this patent does not contain much in the way of novelty.

The samples of caoutchouc produced by these methods of polymerisation, from various raw materials, were examined by Harries, and his results are given below. Isoprene rubber prepared in this way is fairly readily soluble in benzene at ordinary temperatures, but there remains an insoluble residue which can be separated by filtration. The soluble portion, after purification by Harries' method gives, on analysis, the following results :—$C = 86{\cdot}92$, $H = 11{\cdot}87$ per cent. $C_{10}H_{16}$ requires $C = 88{\cdot}2$, $H = 11{\cdot}7$ per cent.

The insoluble residue was heated for two days on the water-bath with benzene, a reflux condenser being used; it swelled up considerably, but only a very small quantity of it passed into solution; on analysis it gave the following results :—$C = 82{\cdot}93$, $H = 11{\cdot}15$ per cent. $C_{10}H_{16}$ requires $C = 88{\cdot}2$, $H = 11{\cdot}7$ per cent. As in the case of polymerisation in presence of acetic acid, autoxidation occurs. The residue retains the properties of caoutchouc yielding a tetrabromide, and a nitrosite which decomposes at 157° to 160° C.

The Elberfeld isoprene caoutchouc, polymerised by heat, vulcanises very well, either by the cold process with sulphur chloride, or by the hot method of Goodyear. Nevertheless, it seems to have a tendency to become a little brittle, if the time of cure is too prolonged.

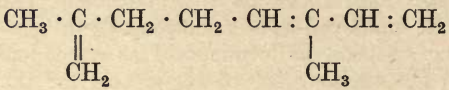
Towards bromine the synthetic caoutchouc behaves like Harries' caoutchouc, but the composition of the bromide is very variable By the Carins method, constant figures could not be obtained, in spite or repeated purification by means of carbon disulphide and petroleum ether; the bromine content varies from 55·92 to 62·42 per cent. Under the influence of heat the colour changes of the tetrabromide are more marked in the case of the synthetic product than in that of natural caoutchouc, and at 150° C., its decomposition point, it becomes completely black.

Towards pure nitrous acid Bayer's synthetic product behaves like that of Harries, readily forming *nitrosite C*, which on analysis gives the following results :—$C = 41{\cdot}74$, $H = 5{\cdot}79$, $N = 13{\cdot}30$ per cent. $C_{10}H_{16}N_3O_7$ requires $C = 41{\cdot}52$, $H = 5{\cdot}23$, $N = 14{\cdot}54$ per cent.

The decomposition of the crude nitrosite occurs at about 130° to 135° C., and that of *nitrosite C* at 145° to 147° C.

The diozonide, prepared in chloroform solution, yields on hydrolysis with water, with slight loss, levulinic aldehyde, levulinic aldehyde peroxide, and levulinic acid. With phenylhydrazine hydrochloride, phenylmethyldihydropyridazine, melting at 193° C., is readily obtained. If, instead of using synthetic isoprene in the Bayer process of polymerisation by the action of heat alone, isoprene prepared from turpentine be employed, the diozonide is obtained in the form of a thick oil which does not vitrify; the loss is much greater in this case than in the preceding one. This must be due to the presence of impurities, such as dimethylallene, in the raw material.

On destructive distillation Bayer's synthetic product behaves like that of Harries. From the crude distillate the same dimeric hydrocarbons, allied to myrcene, can be separated, boiling at 63° to 65° C. at 14 mm., and having in all probability the following structure :—



$$CH_3 \cdot \underset{\underset{CH_2}{\|}}{C} \cdot CH_2 \cdot CH_2 \cdot CH : \underset{\underset{CH_3}{|}}{C} \cdot CH : CH_2$$

with three ethylene linkages, as predicted by Kondakow.

The butadiene caoutchouc, obtained by the Bayer methods of polymerisation, by the action of heat, exhibits some special characteristics, which it will be well to point out.

A large proportion of the raw material is converted into a dimeric terpene, boiling at 36° C. at 23 mm., as in Harries' method, and the compound obtained exhibits the same characteristics as already described.

The caoutchouc separated does not dissolve in any solvent, even after boiling with acetic acid. Analysis shows it to possess the following composition :—C = 86·93, H = 10·96 per cent. C_8H_{12} requires C = 88·88, H = 11·11 per cent.

Autoxidation occurs and the greater part of the caoutchouc is insoluble; this has prevented the preparation and investigation of the tetrabromide, the nitrosites, and the ozonides.

The process of polymerisation by heat alone appears to be little suited to the case of butadiene.

With dimethylbutadiene better results are achieved, and although dimeric by-products are formed, a very fine caoutchouc, supple, elastic, and comparable with isoprene rubber, is obtained. It is more soluble in ordinary solvents and vulcanises more readily.

It can be converted quantitatively into an amorphous grey tetrabromide, difficultly soluble in carbon disulphide. This compound has neither a characteristic melting point nor a decomposition point; it loses hydrogen bromide at about 130° C., and darkens progressively as the temperature is raised.

With nitrous acid it yields a yellow amorphous product, soluble in ethyl acetate, this being a *nitrosite C*. The yield is quantitative, but decomposition does not occur even at 200° C.

On analysis the following figures are obtained :—C = 47·53, H = 6·14, N = 12·44 per cent. $C_{12}H_{19}N_3O_7$ requires C = 45·40, H = 6·04, N = 12·29 per cent.

With ozone, in chloroform solution, an almost quantitative yield of the diozonide is obtained in nine hours. The diozonide is a thick, clear oil, having the following composition :—C = 54·38, H = 7·88 per cent. $C_{12}H_{20}O_6$ requires C = 53·34, H = 7·74 per cent. Two diozonides are actually formed, the one passing into solution more readily than the other, and the less soluble one being the browner of the two. The more soluble boils at 70° to 90° C., and with phenylhydrazine acetate gives a yellow, crystalline precipitate, melting at 119° C.[1]

By the action of boiling water acetonylacetone is formed, which can be converted into acetonylacetonediphenylhydrazone, having the composi-

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[1] Paal, *Ber.*, 1885, 18, 60.

tion:—C = 74·80, H = 7·66, N = 18·87 per cent. $C_{18}H_{22}N_4$ requires C = 73·47, H = 7·48, N = 19·05 per cent.

The aldehyde formed reduces Fehling's solution in the cold; Harries concluded from this that a keto-aldehyde is present in addition to acetonylacetone, but has not been isolated. The readily soluble ozonide gives on hydrolysis, after volatilising the acetic acid:—

(1) A fraction passing over at 60° to 80° C.
(2) A fraction passing over at 80° to 140° C.
(3) A residue.

The first fraction contains the greater part of the product, and this gives immediately, with phenylhydrazine, the diphenylhydrazone of acetonylacetone in crystalline form. The other fractions strongly reduce Fehling's solution.

It is probable that in the polymerisation not only of isoprene but also of dimethylbutadiene, a number of caoutchoucs with different indices of polymerisation (n) are formed—$(C_{10}H_{16})_n$ and $(C_{12}H_{20})_n$,—which on ozonisation give different products. This agrees with Ditmar's opinion; he maintains that the coefficient n is very variable, according to the temperature and the solvent, and that it has never one value only.

In the course of their experiments on butadiene, the Bayer chemists noticed, on attempting to purify this compound by the classical method adopted in the case of terpenes—viz., with metallic sodium—that polymerisation to caoutchouc took place. A similar observation was made by Harries on heating butadiene in a sealed tube at 35° C. for three hours. Weizmann, who had long noticed the action of sodium on terpenes, had in turn pointed it out to Matthews, who also applied the observation to the condensation of isoprene. Lastly, Kondakow claims to have recorded this reaction ten years ago.

In reality priority in this discovery appears to belong to Matthews, and an examination of the facts leads to the following statement of the position.

Perkin says:—"Harries pointed out, in Liebig's *Annalen* (1911, 383, 157-227), the fact that metallic sodium brings about the polymerisation of butadiene, isoprene, and their homologues.

"This discovery was made by Harries towards the end of 1910, and was patented by Bayer at the end of 1911.

"But during the summer of 1910, Dr. Weizmann pointed out to Dr. Matthews, in the course of their work on the synthesis of caoutchouc, the possibility of converting dimethylallene into isoprene by the action of sodium; such cases of isomeric change were not unknown amongst unsaturated hydrocarbons. It was, however, found that the isomeric change which takes place gives rise to isopropylacetylene, and not to isoprene.

$$(CH_3)_2C : C : CH_2 \rightarrow (CH_3)_2CH \cdot C ⋮ CH.$$

This had already been recorded by Faworsky.[1]

"Dr. Matthews then conceived the idea of applying this sodium reaction to isoprene, and with this object he sealed up isoprene and a little sodium in a tube, in July, 1910.

"In the month of August he inspected the tube, and found that the contents had become viscous, and that a notable amount of caoutchouc was

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[1] *J. Russ. Soc.*, 1887, 19, 558.

present. The tube was again examined in September: it then contained a solid mass of amber-yellow caoutchouc. Investigation, which was immediately begun, showed that the sodium behaved towards the isoprene as a polymerising agent of the first rank, and that it behaved in the same way towards the homologues of isoprene. Application for the English patent was made on October 25th, 1910,[1] whereas Bayer's application for the German patent was not made until two months later—viz., on December 12th, 1910 (Ger. Pat. 31,437).

“The reaction received publicity mainly through Harries' paper in the *Annalen* in 1911.[2]

“In this paper Harries states that when butadiene is polymerised (by means of sodium) an isomeric caoutchouc is formed, in which the double bonds are in positions other than those in which they occur in normal caoutchouc. He writes, ‘An observation which I made at the end of 1910 showed that the polymerisation of butadiene is accompanied by a phenomenon which can be explained by the occurrence of isomeric change, the molecular magnitude, of course, remaining constant.

“‘It has, in fact, been found that these hydrocarbons polymerise when they are left in contact with sodium wire in a sealed tube. Butadiene is even converted, at ordinary temperatures, in the course of a few hours; isoprene, according to its degree of purity, is converted, at about 60° C., in 50 to 100 hours, almost quantitatively, without the formation of any dimerides. The sodium remains for the greater part unaltered.’

“The chemists of the Elberfeld works had already seen, it is true, that butadienes underwent some change in presence of sodium, but they had not paid any further attention to the subject.

“The patents taken out by this company, relative to polymerisation by means of sodium, were, therefore, only applied for either as the result of fresh observations, later than those of Matthews, or on the suggestion of Harries, whose work is also later than that of Matthews. On this point, therefore, English priority appears to be very definitely established.

“Kondakow also claimed to have discovered polymerisation by means of sodium, ten years previously. He writes, in the *Revue de chimie pure et appliquée*,[3]:—‘Harries claims for himself the discovery of the catalytic polymerisation of di-isopropenyl by means of sodium, whereas it really belongs to Kondakow. The latter observed the same phenomena when distilling di-isopropenyl, either pure or in admixture, over sodium; however many times the distillation was repeated, the metal always assumed a brown tint, and became covered with a flocculent, viscous precipitate, which was regarded by the author as a compound of caoutchouc with sodium.’

“Having established this fact, he adds[4]:—‘It is evidently impossible to distil this hydrocarbon over sodium with impunity.[5]

“‘On comparing these quotations with the descriptions given by Harries, it is evident that Kondakow was not dealing with a sodium compound, but simply with what has been called sodium caoutchouc, and that it is to him that the discovery of this substance is due.’

“The claims of the Russian chemist are at least singular, and appear to have a minimum of basis. He believed he had a compound of

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[1] Fr. Pat. 437,547; Ger. Pat. 249,868.

[2] *Annalen*, 1911, 383, 157-227.

[3] 1912, 165.

[4] *Actes de l'Université de Jurjew*, 1899.

[5] *J. f. pr. Ch.*, 1899, 59, 295.

divinyl with sodium, but he in no way suggested that this compound was caoutchouc.

"A similar observation had been made by a large number of chemists when they had occasion to distil either derivatives of butadiene or terpenes over sodium, according to the classical method of purification, but that can in no way establish a claim for priority."

It is, therefore, on just grounds that Perkin warmly rejects the claims of Kondakow, whilst at the same time recognising that he has made very important discoveries in the domain of the synthesis.

This point of priority having been settled in favour of Dr. Matthews, it is well to insist on the importance of this discovery, which from the synthetic point of view is of the first order; it leads, in fact, to the establishment of a sure and certain method for the production of caoutchoucs without the use of high temperatures.

Nevertheless, it must be recognised that the structure of the sodium caoutchoucs is not identical with that of caoutchoucs obtained as the result of polymerisation either by heat alone or with the aid of acetic acid.

The caoutchoucs called "*sodium caoutchoucs*," are, then, *abnormal caoutchoucs*, differing in properties from *normal caoutchoucs*. So far a satisfactory explanation has not been given of the differences which exist between the various members of the caoutchouc family, and any attempt to arrive at a rational classification must be postponed until a larger number of facts are available.

A compound containing two conjugated double linkings may polymerise in different ways; three possibilities have already been suggested by Tilden, Harries, and Pickles, and we have explained them.[1]

Consequently it is possible for a given type of caoutchouc to be formed from the fundamental hydrocarbon in different ways, and that the final product may be a mixture of different polymerides.

These differences would be particularly evident in the case of polymerisation by means of sodium, as we shall see in a moment, in summarising Harries' investigations on this subject.

The Bayer patent relating to polymerisation[2] claims the action of the alkali- and alkaline-earth metals, their mixtures, alloys, and amalgams.

According to the text of the specification the reaction is carried out at ordinary temperatures, and no secondary reactions occur:—100 parts of butadiene, condensed by cooling, are left in contact with ½ part of sodium wire in an autoclave. At the end of a day the vessel is opened, and the excess of sodium is destroyed by the addition of water or alcohol. The same result is obtained by treating 100 parts of hydrocarbon with 10 parts of 10 per cent. sodium amalgam. By this process the most varied hydrocarbons, containing a conjugated double linking group, may be treated.

It may be added, as a point of interest, that the specification also mentions the use of ammonium amalgam as a polymerising agent.

The following description is given by Harries of the production of the various abnormal caoutchoucs, of which he has made a thorough study:—

To obtain the sodium caoutchouc derived from butadiene, 9 to 10 parts of the hydrocarbon are heated in an autoclave with half a part of sodium

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[1] A new theory has been propounded by Ruberow, embodying the idea of condensation in spiral form.

[2] Fr. Pat. 434,989, Oct. 7, 1911; Appl. for Ger. Pat. 31,437, Dec. 12, 1910.

wire for three hours at 35° to 40° C.; no pressure is evident on opening the autoclave. The butadiene is converted into a brown mass, which is now washed with dilute alcohol in order to remove the free sodium. A yellow caoutchouc is thus obtained, which is transparent in thin layers, supple and elastic; the yield is 90 per cent., and there is no formation, so to say, of secondary terpene hydrocarbons. Polymerisation may be brought about in the same way at ordinary temperatures, but it is slower; the caoutchouc clings to the sodium wire, and contraction of volume occurs.

Whilst it still contains sodium the caoutchouc is steel-grey in colour, but it becomes yellow on washing with alcohol.

When freshly prepared it is soluble in ether, chloroform, and benzine, but it gradually loses this property after sheeting and becomes tough and very nervy. Then it swells up enormously with solvents, and its solutions are very viscous.

If it be sheeted before it is completely purified, it becomes electrified, a property which would appear to render its employment as an insulator of interest.

It vulcanises readily in the cold, and the vulcanised product is superior in elasticity to all other vulcanised synthetic caoutchoucs. It gives equally good results with hot vulcanisation.

When purified in the usual way it gives on analysis the following figures:—$C = 87{\cdot}92$, $H = 11{\cdot}10$ per cent. C_8H_{12} requires $C = 88{\cdot}89$, $H = 11{\cdot}11$ per cent.

The difference is due to the presence of a second caoutchouc entirely different from the first, as shown by the results of ozonisation. By the action of ozone on a chloroform solution, it yields an oily or a solid, highly explosive ozonide; saturation takes place slowly, requiring from 3 to 10 hours, according to the concentration of ozone in the gas. With concentrated ozone the ozonide is precipitated as a solid white mass, which explodes readily when dry. This property it loses on contact with ether.

The oily ozonide, which is obtained when dilute ozone is used, is not soluble in ether.

The solid ozonide is insoluble in ethyl acetate, in which the oily ozonide dissolves.

The analysis of the soluble product gave the following figures:—$C = 50{\cdot}04$, $H = 6{\cdot}47$ per cent. $C_8H_{12}O_3$ requires $C = 61{\cdot}5$, $H = 4{\cdot}4$ per cent. $C_8H_{12}O_6$ requires $C = 47{\cdot}05$, $H = 3{\cdot}8$ per cent.

These figures show that a portion of the C_8H_{12} has combined with only one molecule of ozone instead of two.

As in the case of compounds containing a conjugated double linking, it is probable that a monozonide is formed, as already observed by Harries.[1] The highly explosive solid product appears to be an oxyozonide, $C_8H_{12}O_4$, which loses oxygen in contact with ether, and is converted into monozonide; it behaves like the ozonide of pinene.

The oily ozonide is a diozonide, and, when dried, forms a solid, white, vitreous mass; like the other ozonide, it does not give the pyrrol reaction on hydrolysis, but that of hydrogen peroxide.

The following figures were obtained on analysis:—$C = 43{\cdot}37$, $H = 6{\cdot}31$ per cent. $C_8H_{12}O_6$ requires $C = 47{\cdot}06$, $H = 5{\cdot}8$ per cent.

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[1] *Annalen*, 1910, 374, 304.

If a solution of the solid ozonide in hot acetic acid be re-ozonised, the product obtained does not yield succinic dialdehyde on hydrolysis.

So far it has not been possible to determine the nature of the products obtained when these ozonides are hydrolysed with water. With nitrous acid, the sodium butadiene caoutchouc gives a yellow precipitate, insoluble in ethyl acetate and acetone, after being in contact with an excess of the acid for a day. This compound cannot be purified, and the *nitrosite C* cannot be obtained. On analysis its composition is found to be variable and not at all normal:—N = 11·91 to 13·18 per cent. $C_8H_{12}N_2O_3$ requires 15·21 per cent. This nitrosite turns brown at 140° C., and black at 230° C.

The bromide is a white powder, with an indeterminate decomposition point; it is soluble with difficulty in carbon disulphide, and is precipitated from the solution by light petroleum. On analysis it gives:—Br = 68·74 per cent. $C_8H_{12}Br_4$ requires Br = 74·7 per cent.

This bromide, therefore, seems to be a mixture of tetra- and dibromide.

According to these analytical results, sodium butadiene caoutchouc seems to be made up of several species of caoutchouc, differing from one another, in all probability, in molecular structure.

Isoprene in contact with metallic sodium is converted much more slowly into caoutchouc than butadiene; in order to obtain a quantitative yield it is necessary to heat it in an autoclave for 50 hours at 60° C. in contact with sodium wire.

Isoprene obtained by destructive distillation and purified seems to behave best in this connection.

The product of the conversion is very tough and difficult to remove from the autoclave, and it is often necessary to dissolve it and reprecipitate it by means of alcohol; it is very elastic, and on stretching gives wide bands, like Para. It is readily soluble in the ordinary solvents and vulcanises equally well by the hot or cold process. On analysis it gives:—C = 87·97, H = 11·66 per cent. $C_{10}H_{16}$ requires C = 88·16, H = 11·84 per cent.

Although it has this composition, the study of its derivatives shows it to be a different substance from normal synthetic caoutchouc. It should, moreover, contain a small quantity of normal rubber, as the result of a certain amount of "normal" polymerisation—that is to say, through the influence of heat alone.

When ozone is passed into a solution in carbon tetrachloride to saturation, an operation which takes 10 hours to complete, a white gelatinous precipitate is formed, which, after filtration through glass wool and washing with ether, becomes soluble and friable.

The solid ozonide is almost completely soluble in ethyl acetate, and is precipitated from solution by light petroleum as a thick oil, which after drying solidifies rapidly, and can then be powdered.

It is less explosive than the ozonide of butadiene, and more so tha that of normal isoprene caoutchouc. On analysis it gives:—C = 54·82, H = 7·72 per cent. $C_{10}H_{16}O_6$ requires C = 51·71, H = 6·94 per cent. It is a mixture of the di- and monozonides. If ozone be passed into a chloroform solution a thick colourless oil is obtained, which, after purification from ethyl acetate and drying, gives a solid, white pulverulent mass. It burns very briskly, and gives the hydrogen peroxide reaction after boiling with water. Analysis shows it to be a very pure diozonide:—C = 51·44, H = 7·08 per cent. $C_{10}H_{16}O_6$ requires C = 51·71, H = 6·94 per cent. The molecular weight as determined by Raoult's method is 266 to 262, the calculated value being 232.

The ozonides just described behave quite differently from the diozonide of natural caoutchouc, when hydrolysed by water or acetic acid. They do not give the pyrrol reaction; they are only sparingly soluble in water and hydrolyse with difficulty, giving only a very small quantity of levulinic aldehyde—identified by the formation of its phenylmethyldihydropyridazine—when dilute acetic acid is used. Moreover, brown oils are always formed in the process, and decompose on distillation.

From these observations it is very clearly evident that the sodium caoutchouc derived from isoprene differs from the normal synthetic product as much as from natural rubber.

On attempting to prepare the *nitrosite C*, two compounds are obtained, one of which, the more abundant, is difficultly soluble in ether and soluble in acetone, whilst the other is insoluble in both these solvents.

The former is a yellowish-white powder, which browns slightly at 170° C., and becomes dark brown at 180° C., undergoing no further change of colour up to 260° C. On analysis it gives:—$C = 48{\cdot}69$, $H = 5{\cdot}56$, $N = 12{\cdot}62$ per cent. $C_{10}H_{16}N_2O_5$ requires $C = 49{\cdot}20$, $H = 6{\cdot}50$, $N = 11{\cdot}50$ per cent.

The figures do not agree with any nitrosite formula. The bromide is a white powder, soluble in carbon disulphide, and precipitated from solution by light petroleum. On analysis it gives $Br = 68{\cdot}05$ per cent. $C_{10}H_{16}Br_4$ requires $Br = 70{\cdot}14$ per cent. This bromide has many points of similarity with the bromide of normal synthetic caoutchouc. The polymerisation of dimethylbutadiene by means of sodium is effected under the same conditions as that of isoprene, the process requiring 10 to 12 days at 60° C. The mass obtained is brown in colour, and is almost completely soluble in ether, from which it is precipitated by means of alcohol. The insoluble portion is white, and remains insoluble in all solvents.

This product seems very different from the normal synthetic product, and reminds one of guttapercha.

By the action of ozone on a chloroform solution, a thick oil is obtained, which, on hydrolysis, gives the hydrogen peroxide reaction, and yields a little acetonylacetone.

The sodium caoutchouc would, therefore, seem to contain a little of the normal synthetic product, formed by simple heat polymerisation. The composition of the other products of hydrolysis has not yet been determined.

The nitrosite is, for the greater part, soluble in ethyl acetate, from which it is precipitated by light petroleum; it has no characteristic decomposition point. On analysis it gives:—$C = 47{\cdot}59$, $H = 6{\cdot}13$, $N = 11{\cdot}0$ per cent. $C_{12}H_{19}N_3O_7$ requires $C = 45{\cdot}40$, $H = 6{\cdot}04$, $N = 13{\cdot}25$ per cent.

The bromide is white, pulverulent, soluble in carbon disulphide, and precipitable by light petroleum. At 130° C. it loses hydrogen bromide, and it does not melt at 200° C. It contains, on analysis, $Br = 62{\cdot}57$ per cent. $C_{12}H_{20}Br_4$ requires $66{\cdot}08$ per cent.

These facts are sufficient to show that in the case of dimethylbutadiene, as in that of its lower homologues, the sodium caoutchouc is a totally different thing from the normal synthetic product, although the two possess most of their physical characteristics in common.

In the Matthews process isoprene and its homologues are heated in an autoclave at 60° C. for several days in contact with sodium cut up into slices.

A brown mass is obtained from which the caoutchouc is precipitated on the addition of alcohol. The caoutchouc is then washed with alcohol, and steamed in order to drive off the excess of the latter, together with any unchanged hydrocarbon retained by the polymeride.

The Bayer works have made an application for a German Patent, No. 35,438, dated November 12th, 1910, in which they claim a method of preparation based upon the treatment of erythrene, its analogues and homologues, with substances generally regarded as inert, such as starch, albumen, urea, and glycerin. Thus, 100 parts of butadiene are left in contact with 1 or 2 parts of starch, in a closed vessel, for several months; the reaction is greatly assisted by heat.

Synthetic caoutchouc can be vulcanised. The vulcanisation thereof forms the subject of a patent application by the Bayer works,[1] entitled "Process for the Preparation of Masses similar to Vulcanised Rubber."

As an example of the method, 5 parts of synthetic butadiene caoutchouc is dissolved in 100 parts of benzol, and a solution of 1 part of sulphur chloride in 50 parts of carbon disulphide is added to it. After two minutes the product is poured into alcohol, when a highly tenacious and resistant substance is obtained. Vulcanisation may also be effected by incorporating 15 parts of flowers of sulphur with 50 parts of synthetic caoutchouc, giving the mass any desired form, and then heating it for four to five hours at 150° to 160° C.

In their patent 248,399 of March 23rd, 1911, the Bayer works describe a method for the acceleration and completion of the polymerisation of the hydrocarbons in different rubbers. This method consists in carrying out the polymerisation in presence of ready-formed caoutchouc which forces the reaction.

It would seem that there is some analogy between these methods and Reynaud's process. The reaction has, moreover, been previously recorded by Eduardoff.

By way of example of the Bayer process, one part of liquefied butadiene may be mixed with one part of caoutchouc obtained in a previous operation, and polymerised in presence of sodium wire. Other substances which assist polymerisation, and the use of which has already been referred to, such as formic acid, creosote, and benzol, may also be added.

Taking up the preparation of the normal synthetic caoutchouc, obtained from methylisoprene by spontaneous polymerisation, as described by Kondakow in 1901, the Bayer works found that the insoluble caoutchouc thus obtained is transformed on treatment with basic agents such as aniline, ammonia, or dimethylamine.

The Badische Anilin und Soda Fabrik[2] obtain caoutchouc by the action upon isoprene or its homologues of quite small quantities of mineral or organic acids, or of substances having an acid reaction, or again of sulphur.

Previously,[3] this company had proposed to prepare caoutchouc by heating isoprene with or without the addition of neutral or alkaline substances, or substances functioning as alkalies.

Thus isoprene is polymerised by heating it for 20 hours at 120° C., or by heating it with 10 per cent. alcoholic soda at 100° C., which is identical with Kondakow's first process, applied to the case of methylisoprene.

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[1] Application for Ger. Pat. 29,664, April 6, 1910; Fr. Pat. 427,299.

[2] Fr. Pat. 434,587, Sept. 26, 1911.

[3] Fr. Pat. 417,170, June 15, 1910; Ger. Pat., March 19, 1910.

In order to prepare caoutchouc from dimethylbutadiene[1] the Badische Company proposes to heat the hydrocarbon in an autoclave at 100° C., for a variable length of time, with water, alcohol, ether, or a solution of common salt.

Hodgkinson[2] converts isoprene and its homologues into caoutchouc by the action of sodamide, and of nitrides such as those of magnesium and iron, in the absence of oxidising agents. Black and Morton[3] claim that the various hemiterpenes, as well as carbohydrates like inositol, dambose, and bornose, are converted into a substance similar to caoutchouc, under the influence of micro-organisms present in the latex-yielding plants.

Isoprene, in particular, and "mortonene," a hemiterpene isolated by Black and Morton from the products of dry distillation of rubber resins, notably those of Jelutong, are converted into rubber under the influence of micro-organisms found in *Landolphia;* the same is true of inositol in presence of cultures obtained from *Hevea.*

These various organisms are cultivated at 30° to 35° C., on the above-mentioned substances, and the conversion is accelerated by the addition of magnesium pyrophosphate.

In investigating the action of heat on isoprene, Lilley[4] noticed that this hemiterpene can be converted into a terpene, to which he gave the name *mesoprene.* When this compound is poured in thin layers on to water containing free acids or acid anhydrides, it gradually solidifies on warming to 100° C. This solidification can be effected still better by working *in vacuo,* especially in presence of dissociable salts.

Polymerisation may also be determined by means of a current of sulphur dioxide, or of hydrogen chloride.

Latterly various processes have been brought forward, either by companies which have already been working at caoutchouc synthesis, thus consolidating their initial discoveries, or by new investigators. There is nothing of major interest in these, and not many new ideas.

Thus the Bayer Company[5] has patented the polymerisation of isoprene and its homologues by the action of electrical energy, a process which had already been brought forward by Collie, and has been referred to above.

The Badische Company[6] proposes to heat isoprene or its homologues in presence of cerium sulphate, blue vanadium salts, or oxidisable metals, and thus obtain a substance analogous to caoutchouc.

Schering[7] brings about the polymerisation of butadiene and its derivatives by heating them with an organic anhydride, as, for example, acetic anhydride. This process is evidently very similar to that of Harries, or of the Badische patents, in which formic acid is used as a condensing agent.

Heinemann[8] treats isoprene and its homologues with albuminoid substances, such as peptones, albumin, and keratin, and thus converts it into caoutchouc. A similar idea had already been put forward by the Badische Company. Wallace,[9] like Morton and Black, but prior to them, treated isoprene with the micro-organisms present in natural rubber and in latex. The fermentation processes, in which the hemi-terpenes are acted upon, seem very much open to discussion; if the mechanism of such a change is

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[1] Eng. Pat. 14,281, of 1910.

[2] Eng. Pat. 9,219, April 16, 1910.

[3] Eng. Pat. 27,398, Nov. 24, 1909.

[4] Eng Pat. 29,777, Dec. 14, 1909.

[5] Fr. Pat. 432,222.

[6] Fr. Pat. 440,173.

[7] Fr. Pat. 433,825.

[8] Fr. Pat. 439,101.

[9] Eng. Pat. 15,299, of 1909.

conceivable when a sugar such as dambose or inositol is employed, one cannot see, on the contrary, how bacterial action could bring about the condensation of C_5H_8. Silberrad[1] claims to have obtained a special kind of caoutchouc containing nitrogen, which he calls *pyrido-caoutchouc*, by the polymerisation of substances such as the product of the condensation of acroleïn with methylamine. Although few details of Silberrad's experiments are available, this attempt is very interesting, and it might be so industrially if the polymerisation can be readily effected, and if the polymeride has the properties of natural rubber, for the source of the raw materials is abundant and cheap. Silberrad's process would appear to deserve a very careful examination.

Silberrad, Allebrook, and Docherty have exhibited, under various circumstances, samples of caoutchouc which they claim to have obtained by various synthetic methods, as to which, unfortunately, they have furnished no information. We can, therefore, only mention them by the way.

Lebedew, whose researches we have already summarised, in collaboration with Skavronskaia,[2] pursued investigations on the formation of terpene derivatives in the course of the preparation of normal synthetic caoutchouc.

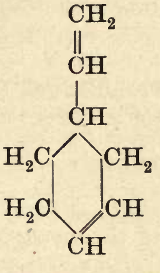
On polymerising divinyl, by heating it at 150° C. for ten days, these chemists obtained, as did the Bayer chemists, a solution of a caoutchouc in a dimeride produced in the first stage of the condensation of butadiene.

It was of interest, from the point of view of the study of polymerisation, to examine this dimeride.

It can be isolated by distillation under a reduced pressure of 100 mm., in presence of carbon dioxide.

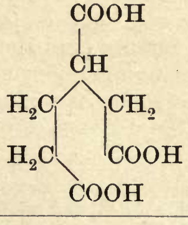
It is a colourless liquid, boiling at 65° to 66° C. at 100 mm., and at 129·5° to 131° C. at 760 mm. Its density ($d_{4°}^{20°}$) is 0·832 ; it oxidises readily in the air.

According to Lebedew and Skavronskaia, it is *ethenyl*-1-*cyclohexene*-3—



It is reduced by hydrogen, in presence of platinum, at ordinary temperatures, to ethylcyclohexane.

It yields a tetrabromide which melts at 69·5° to 70·5° C. On oxidation it is converted into an open-chain tricarboxylic acid—viz., *β*-carboxyadipic acid—



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[1] *Gummi Zeit*, 1911, 25, 1958.

[2] *J. Russ. Soc.*, 1911, 43, 1124

The caoutchouc obtained dissolves, with some difficulty, in carbon tetrachloride, leaving an insoluble residue.

With ozone it gives a gelatinous ozonide, which dries to a colourless, highly explosive powder, insoluble in all solvents. It is decomposed by water with difficulty, and amongst the products of hydrolysis succinic acid and succinaldehyde are found. Its composition would be analogous to that of the diozonide of natural caoutchouc.

In order to complete our examination of the synthesis of caoutchouc, we must refer, in a few words, to the "pseudo"-synthesis of Reynaud and Rouxville, although, with great modesty, the latter disclaims any pretensions to an actual synthesis, but simply claims to have devised a process for regenerating old caoutchouc.

Although they present themselves in different aspects, the two processes are very much allied, and have many points in common. Both of them aim at the conversion of turpentine, if not into caoutchouc, at least into a closely related substance which can be vulcanised. The earlier of the two is Rouxville's process,[1] and this has been investigated very thoroughly by Masselon, to whose work the reader is referred.

Reynaud's process [2] consists in absorbing a certain amount of turpentine in powdered rubber, and then treating the mass with successive solutions of sulphuric acid of gradually increasing strength, and finally with 66° acid and hydrochloric acid. This process lasts from 18 to 20 days, and in the course of it the mass, which is at first viscous, gradually solidifies to a product somewhat similar to caoutchouc in physical properties, which, after being carefully washed and neutralised, can be vulcanised. No trace of turpentine can be driven off by a current of steam, and the terpene has, therefore, evidently been polymerised. The product gives a bromide and a nitrosite, but does not give Harries' reaction with ozone, and very small quantities of levulinic aldehyde and acid, arising doubtless from the original rubber employed, are produced.

Reference to the work of Bouchardat and Lafon would lead one to suppose that the substance is a mixture of colophene and rubber.

. . . .

The account given above, which, although lengthy, is unfortunately still incomplete, will give an idea of the enormous amount of work which has been carried out in recent years, with a view to arriving at a practical solution of the synthetic rubber problem.

Although it has not yet been possible to achieve a complete result, nevertheless the outlook begins to get clearer, and the data of the problem have been definitely settled. Two solutions, each of which has within it the possibility of being industralised, have been put forward; the one by the chemists of the Bayer works, Hoffmann and Coutelle, the other by the English group, under the direction of Perkin, Strange, and Matthews.

The question of the raw material employed plays a very important part in the realisation of the synthesis, for, as we have said repeatedly, it must be abundant and very cheap. The derivatives of coal-tar, phenol, and cresol,

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[1] Fr. Pats. 356,716, 375,709, 378,231, and additions 9,374, 9,376, 378,801.

[2] Fr. Pat. 419,860, April 23, 1910.

to which the German chemists have directed their attention, answer these requirements, but the method of treatment which they have adopted in order to obtain caoutchouc from them is lengthy and delicate. It comprises, in fact, no less than five operations in passing from the hydrocarbon to the divinyl compound, and necessitates, moreover, a costly methylation process.

The higher alcohols, to which Perkin and his collaborators have recourse, lend themselves to an easier method of treatment, since they require only three operations, and the use of such auxiliary substances as hydrochloric acid, chlorine, lime, and soda, all of which are cheap.

The economic value of this method depends absolutely upon the efficient working of Fernbach's fermentation process, about which scarcely anything is known. On Perkin's own admission it yields mainly butyl alcohol, from which it is only possible to obtain butadiene caoutchouc, a product somewhat different from natural rubber, as we have seen.

The same remark applies to the preparation of acetone: if Fernbach's method gives the yields which have been published, this compound would permit of the preparation, easily and economically, of pinacone, and, from it, of dimethylbutadiene.

In the English synthesis, the whole thing, therefore, from an economical point of view, rests upon the Fernbach processes and their yields. Hence it is possible to understand in some measure the reserve with which this method has been received, for Fernbach processes have not yet the sanction of practical working.

We have, however, tried to show that, apart from the direct conversion of starch, as carried out by Fernbach, an abundant source of higher alcohols could be found in the breaking down of the amino-acids which are present in large quantity in distillery vinasses, and in the residuals of sugar refineries and starch mills, and that quite a number of processes have been worked out, and have given practical results on an industrial scale.

On the other hand, the employment of isopentanes obtained from petroleum, both from the point of view of the preparation of adipic acid and from that of the direct action of halogens, is surrounded with great interest, as Perkin has not failed to notice.

Lastly, there is the raw material acetylene from calcium carbide, which, it seems to us, in spite of the opinion to the contrary held by Harries, ought to form one of the future bases of synthetic caoutchouc, not by employing it direct, and attempting to combine it with ethylene, as in Heinemann's process but rather by using it for the preparation of acetaldehyde.

Calcium carbide is cheap, and can be obtained in unlimited quantity, since its production only involves the use of carbon, lime, and electric current. The acetylene prepared from it is converted quantitatively into aldehyde by the catalytic action of mercury salts, and this aldehyde, obtained more economically than the higher alcohols of the Fernbach process, and also than phenol or cresol, may lead—

(1) Directly to butadiene caoutchouc, through aldol, followed by reduction and chlorination.

(2) To acetic acid by oxidation, and thence by the method of Sabatier and Senderens to acetone, pinacone, and consequently dimethylbutadiene caoutchouc.

From the standpoint of polymerisation the problem seems to be completely solved, and the methods worked out; Matthews' sodium process, Harries' acetic acid process, and Hoffmann and Coutelle's direct-heating process are capable of being actually applied industrially, without any great technical difficulties.

It now remains to be seen whether the synthetic caoutchoucs obtained by these methods will show in use the same properties and the same quality as the natural product.

It is impossible here to reply definitely to this query, because only actual experience can decide the point; and again this will have to last for years in order that the similarity in behaviour of the two products in actual use may be demonstrated.

It must not be forgotten, in fact, that the synthetic caoutchoucs, especially the sodium products, do not appear to have the same structure as the natural product; the dissimilarity of the products of hydrolysis of their ozonides appears to be a positive demonstration of this hypothesis, which may be full of consequences—favourable as well as unfavourable—for the synthetic products.

In short, with isoprene—that is to say, with the raw material which is most costly and most tedious to produce—a normal synthetic caoutchouc is obtained, which from its chemical behaviour appears to be completely identical with natural caoutchouc.

With butadiene and dimethylbutadiene, whether one considers the normal synthetic products or the sodium caoutchoucs, one is dealing with new products, the structure of which is evidently different from that of the natural product, and which are, moreover, very difficult to know, on account of their colloidal nature. Although their manufacture appears to be easier and more remunerative than that of synthetic isoprene caoutchouc, we are as yet unable to say whether the final products will give the results expected of them—viz., results similar to those given by natural caoutchouc.

It was thus with reason that the *India Rubber Journal*, subsequent to Perkin's communications, wrote:—" Butadiene caoutchouc, derived from a compound containing four carbon atoms, or dimethylbutadiene caoutchouc, derived from a compound containing six, must necessarily be different from natural caoutchouc, derived from isoprene, which contains five.

" Five carbon-atom caoutchouc we know, but four or six carbon-atom caoutchoucs we do not know. What results will these types give? Nobody knows."

It is, therefore, necessary to put them to exhaustive tests patiently, and whilst waiting for the results, to seek to perfect the methods of production of isoprene, which is itself capable of yielding a perfect synthetic product.

One can understand, therefore, that with such uncertainties before his mind, one of the men who knows most about the synthesis of caoutchouc, Dr. Duisberg, director-general of the Bayer works, should, in his lecture on the synthesis of rubber before the Congress of Applied Chemistry in New York, 1912, have put forward the following conclusions, full of reserve:—

" If you ask me to reply, in all honesty and truth, as to when synthetic caoutchouc will bring with it the millions which certain prophets see in its exploitation, I must say that I do not know.

"Certainly not to-morrow, although synthetic rubber should appear on the market in a very short time, and I hope to live long enough to witness this fresh triumph of Art over Nature."

Duisberg thus revealed the fact that the problem is without doubt well advanced, and that its solution is at hand, but that it is not yet definitely, and certainly not practically found.

As between the cup and the lip, so between the laboratory and the works there is still room for some miscalculation and much work.

SUBJECT INDEX.

AUTHOR INDEX.

PLACE INDEX.

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2