RUBBER MANUFACTURE

SIMMONS

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RUBBER MANUFACTURE

THE CULTIVATION, CHEMISTRY, TESTING, AND MANUFACTURE OF RUBBER, WITH SECTIONS ON RECLAMATION OF RUBBER AND THE MANUFACTURE OF RUBBER SUBSTITUTES

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TO

MY PARENTS

who by their sacrifices made it
possible for me to obtain
an education.

PREFACE

The author has attempted to give in this volume a brief but complete survey of the Rubber Industry. The production of crude rubber, including the methods in use for collecting both wild and plantation rubber, are carefully described as well as the processes in use for coagulating and curing the crude rubber.

The manufacture of numerous inorganic fillers and their proper use in rubber compounding are given in full as well as the various processes employed for fabricating rubber goods. The apparatus used in all parts of the industry is fully illustrated and described.

The chemical and physical properties of the latex and rubber, including the production of synthetic caoutchouc, are fully discussed. Chapters have also been included on the chemical analysis and physical testing of rubber and its compounds and the various theories of vulcanization.

While the attempt has been made to present the technical features of the subject in a scientific manner so that the volume will be of value to students of this subject, it is believed that a large part of the volume will be of interest to the non-technical reader. Both classes of readers will no doubt be interested in the attempts to point the way for the future development of this most important product.

H. E. S.

Akron, Ohio,
February 1, 1921.

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CHAPTER I

The History of Caoutchouc

Before starting this series of chapters, it seems to me both necessary and interesting to take a brief glance into history and obtain a little knowledge as to when and by whom this important article of commerce was first found. It is my purpose to deal principally with the rubber industry as it is at the present time, yet to omit mentioning the discovery of this substance would be unfair to the pioneers, and would also render a work of this nature incomplete.

It has been stated that the first reference to rubber occurs in the work of a Spanish writer of Madrid in 1536, but M. L. Tillier points out that P. Martyr d'Angliera in 1525 published a description of some rubber playing balls seen by him in Mexico.

Another Spanish writer describes the same article as made " from a black resin, obtained from a tree called by the natives Ulaquhuil." In this connection it will be well to state that in parts of Mexico and Central America even to-day the Castilloa elastica is known as the Ule tree.

According to Morris, the first record of india-rubber was made soon after the discovery of the New World by Columbus. The Old World rubbers were still unknown. Columbus, on his second voyage, noticed the inhabitants of Hayti playing with a ball made from the resin of a tree. It is interesting to note that the game which the natives played with these balls is still played in these regions and in fact, modern explorers have become aware of the presence of rubber yielding trees simply by observing that this game was being played. Antonio de Herrera Tordesillas, a Spanish historian in 1601, in his " General History of the Voyages and Conquests of the Castillians " while speaking of the conquests in Mexico, mentions certain trees which, when punctured, yield a milk which becomes converted into a gum with a very fine smell.

Father Xavier de Charleroix of the Society of Jesus, 1682-1761, describes the Batoa, a species of ball of a solid matter but extremely " porous and light. It soars higher than other balls, falls to the ground and rebounds higher than the level of the hand which it quitted. It falls to the ground and rebounds once more although not to such a height this time, and the height of the bound is gradually diminished."

Whatever the date may be which marks the first recognition of this important article in civilization, we at least must give credit to the Spanish and Portuguese explorers of the West Indias as being the first to observe it and record it in their literature.

The French were the first to make any scientific study of rubber bearing plants. The Academy of Science of Paris in 1731 sent an expedition to South America under the guidance of La Condamine and Bougner. In 1736, La Condamine sent back to the Academy a resinous mass under the name of " caoutchouc " and this information:

> "There grows in the province of Esmeraldas, a tree called by the natives of the country 'Heve'; there flows from it, by simple incision, a liquor, which hardens gradually and blackens in the air. The inhabitants make flambeaux of it, which burns very well without wicks, and gives rather of a fine light. . . . In the province of Quito, sheets of linen are coated with it, and are used for the same purpose as we use waxcloth. . . . The same tree grows along the banks of the Amazon and the Mainas Indians call

> the resin which they extract from it 'cahuchu' (pronounce caoutchouc). They make boots of it, which do not draw water, which after being blackened by being held in the smoke, have all the appearance of leather. They coat earthen molds in the shape of a bottle with it, and when the resin has hardened, they break the mold and force out the pieces through the neck and mouth; thus they get a nonfragile bottle, capable of containing all kinds of liquid."

He also mentions a peculiar use which one of the tribes made of this india-rubber:

> "The use which is made of this resin by the Omaguas, in the middle of the American continent, on the banks of the Amazon, is still more singular; they make bottles of it in the shape of a pear, to the neck of which they attach a fluted piece of wood. By pressing the bottles the liquid which they contain is made to flow out through the fluted piece of wood, and by this means these bottles become real syringes."

That is the origin of the name given by the Portuguese to the tree which yields this resin, Pao de Ciringa (syringe-wood), and of seringueiros to the resin collectors.

At this point La Condamine had to give up his pursuit of this peculiar substance and devote his time to his own profession, for he was a doctor of medicine and an eminent naturalist. At this time he came in touch with Fresneau, the French engineer located at Cayenne, who seemed to grasp the importance of this substance and took up the work where La Condamine had abandoned it. After great labor and hardship he succeeded in finding these trees and noticing how the natives proceeded to obtain this resin, he sent the following communication to La Condamine:

> "They commence by washing the foot of the tree; then they make with a bill-hook, longitudinal but rather oblique incisions which should penetrate the whole thickness of the bark, taking care to make them, one above another, so that the flow from the top incision falls into the one underneath, and so on until the last one at the bottom of which a leaf of the Balizier (an American reed) is placed, which is made to hold the liquid by potter's earth, so as to lead the juice into a vessel placed at the foot of the tree.
>
> "To utilize the milky juice of the trees which I have mentioned, a mold is made of potter's earth, according to the shape of the vessel which it is intended to make, and, to hold it more conveniently, a piece of stick is inserted in the place which is not to be coated with the milky juice. An aperture is thus secured through which the potter's earth may be afterward expelled, by introducing water to soften it. Any one mold being shaped, polished, and softened with water, it is coated all over with milky juice by means of the fingers, after which this coating is exposed to a dense smoke, where the heat of the fire hardly makes itself felt, keeping constantly turning it, so that the juice may be spread equally over the mold, and taking good care that the flame does not reach it, which would cause the milky juice to boil, and thus to form small holes.
>
> "As soon as a yellow color is seen, and this first coating is no longer tacky to the fingers, a second layer is applied, which is treated in the same way, and so on with the other coats, until it is judged to be sufficiently thick, and then it is kept longer over the flame so as to evaporate the whole of the moisture, until but the elastic resin remains. . . . With this juice and linen sheeting, tarpaulins, pump hose, divers' clothing, bottles, sacks for containing campaigning biscuit, etc., may be made, without fear of this material imparting any bad smell; but all of these things can only be executed on the spots where the tree grows, as these juices soon lose their fluidity."

In 1762 the French botanist Fuset-Ablet started for Guiana and two years later he published "The Flora of Guiana," and in this he described a tree which he called *Hevea Guyanensis.*

In 1798 James Howison determined the name of an elastic gum vine, the species which later on was called *Urceola elastica.* This tree was the chief source of supply from the East prior to the introduction of that from the *Ficus elastica.* It was discovered on the island of Penang. While clearing a way through the jungle with cutlasses, the blades became covered with a juice which hardened and had the appearance of india-rubber. The source of this juice was found to be a vine about as thick as a man's arm, which ran along the ground for great distances, rooted at its joints and also climbed the highest trees. It was thought to be a species of Hevea, with which it is often confused even to this day. This juice was also used by the natives to waterproof different articles.

It is reported that in 1755 the King of Portugal, having heard of the waterproofing material of the Indians, sent several pairs of his royal boots to Para in order that they might be covered with rubber.

Priestley is credited with having given this substance the recommendation to use for effacing pencil marks, and from this it was called " india-rubber."

W. H. Johnson gives us the derivation of the word *caoutchouc* as coming from *caucho,* which in turn comes from *cao,* meaning wood, and *o-chu,* meaning to run or weep.

In this work I shall use the term " caoutchouc " when reference is made to the pure hydrocarbon while I shall use india-rubber as a term for the crude product whether raw or manufactured.

When we realize that it was toward the end of the eighteenth century before rubber was introduced into Great Britain the wonderful advance made in this length of time makes it impossible for us to prophesy what the future has in store along this line.

CHAPTER II

Rubber of the Amazon Basin

As stated in Chapter I, the French were the pioneers in obtaining exact information in regard to the South America rubbers. It was the expedition of de La Condamine and Bougner, from the Paris Academy of Science, in 1731, that sent the first reports dealing with rubber in Peru and Brazil back to the Eastern World.

In 1736 de La Condamine sent home samples of rubber, and referred to the fact that in the province of the Esmeraldas there occurred a tree called by the natives *Hevea,* and that they obtained from it a milk white liquid, which gradually hardened and blackened in the air. He also mentioned that in the province of Quito the natives coated linen with this material, and that the same tree grew on the banks of the Amazon; also that the natives made water tight boots from it, which had the real appearance of leather, after having been blackened by means of smoke. He goes further and says that the natives made some moulded goods from this material. From his writings we find several of the terms still in use.

I mention this simply to give some idea as to the length of time civilized man has been acquainted with this important substance, and in what condition and state of development he found it.

In the beginning it is well to define a few of the terms which will be used and describe briefly the labor condition which prevails throughout nearly all of the South America rubber regions.

Thus far very little of the vast territory bearing these rubber producing trees has been even explored, to say nothing of their being available for tapping. It is estimated that there are at present 300,000,000 virgin trees in this territory.

Tracts of this rubber producing region are obtained by individuals or companies on lease from the state, and the working of any area which has not been surveyed by the state is punishable under the law of theft. The number of leases and sub-leases is considerable. From the report of the Commission of Economic Expansion in Brazil during the year 1906-07 there were organized fifty-two such companies with a capital of two millions sterling. These concessions are termed *scringals,* and are usually computed according to the number of *estradas* running through them. The *estradas* are paths running

FIG. 1

through the forest in such a way as to lead past from one hundred to one hundred and fifty trees. Sometimes the trees are some distance apart, but generally they are found in groups of from two to six.

The *seringueiro* is the name applied to the one taking care of a *seringal*. The *seringueiros* are mostly natives of the states of Ceara and Maranhao. Due to the high death rate and the great number of desertions, it is necessary to provide about eighty laborers for a *seringal* on which fifty could actually do the work. One *seringueiro* is supposed to take care of two *estradas* after they are opened up and put into operation.

The cost of financing a *seringal* is rather high, as Sandmann has estimated it costs about $25,000 to put into operation a *seringal* of one hundred *estradas*, that is, from 10,000 to 15,000 trees. This will buy the outfit necessary, cut the paths, build the huts and factory, and also allow for a little incidental expense.

The *patrao*, the owner or sub-owner of a *seringal*, very seldom finances his own property. He obtains the advances from the large dealers and export firms at Para and Manaos. They are termed *aviadores*. Thus it will be seen that the financing is really done by the *aviadores*, and they hold a mortgage on the *patrao*, who in turn mortgages the labor of the *seringueiro*.

The average yield of a six months' season of an industrious *seringueiro* is about eight hundred pounds of rubber. When he has paid his advances to the *patrao* there remains a profit of about $250 to $300. This is hardly sufficient to support his family at the seat of operations during his absence on the *seringal*. It is fortunate for him that the streams and forest furnish fishing and hunting almost sufficient to support him, but because of the poor way in which the food is prepared and the unhealthy climatic conditions, there is much sickness and the mortality is high. The occupation of a *seringueiro* is not an enviable one.

Varieties

In the Amazon Basin we find the order of *Euphorbiaceae*, the most important genus of which is the *Hevea*, and here we find many different species, the most important one being the *Hevea brasiliensis*, the species from which the widely known Para rubber is obtained. This species is found over a large part of northern South America but principally in the areas watered by the Amazon and its tributaries, in the states of Para, and Amazonas, in Brazil. This is the species from which the Eastern plantations have been largely propagated. It is a large tree, in its natural state often attaining a height of one hundred feet and a diameter of forty inches.

There are several varieties obtained from the *Hevea brasiliensis*.

Fig. 2—Rubber Gatherers Dressed for a Holiday

We find two main regions in which Fine Para is prepared, the "Islands" at the mouth of the Amazon River; and the "Up-river" regions near and above Manaos. "Islands" rubber is generally known as "soft-cure," and "Up-river" as "hard-cure."

The scraps of rubber adhering to the bark of the trees and coagulating cups are compressed into irregular forms and sold as "Negroheads." "Up-river Negroheads" are generally called "scrappy" and "Islands Negroheads" are called "Sernamby." There is another variety of negrohead, the Cameta, coming from a district of that name in Southwest Para.

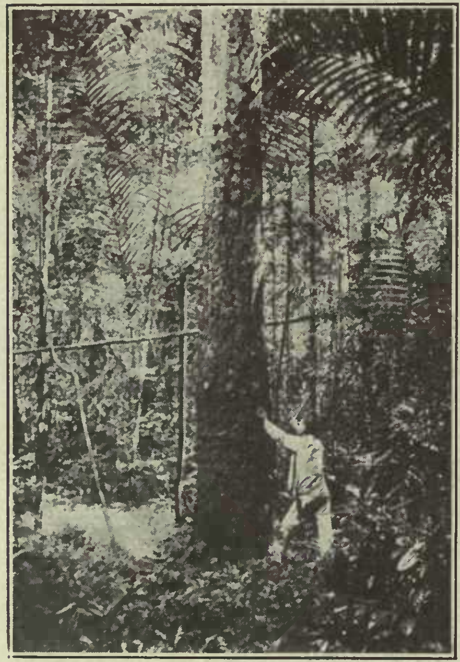


Fig. 3—Tapping Wild Rubber Trees

This same species supplies from the Province of Matto-Grosso, in Brazil: the Matto-Grosso, Fine and Entrefine; Matto-Grosso, Virgin Sheets, and Matto-Grosso, Negroheads.

From Bolivia we obtain Bolivian, fine, medium and coarse; also Mollendo, fine, medium and coarse. These are also obtained from a species of *Hevea.*

From Peru we get Peruvian (fine. coarse or scrappy), likewise of the *Hevea.*

From Ecuador we obtain a new species, the *Sapium,* several varieties of which are: Ecuador scrap, sausage; Esmeralda sausage, Caucho blanco, and Caucho negro.

Confused with these last two we often come in contact with a variety known as Caucho Balls which is of the *Hevea brasiliensis.*

During the last quarter of a century large quantities of Caucho have been found in the districts of Obidos, Tocantins, Xingo, and Tapajos rivers. This supply is likely to be exhausted due to the fact that the natives gather this latex by cutting down the tree and then bleeding it.

There are some seventy varieties of the *Manihot* rubber but we shall call attention to but two, the Ceará and Maniçoba which grow in a relatively poor soil and at altitudes where most other rubber producing trees cease to exist. The bulk of these rubbers come from the Province of Ceara, Brazil. There is some difficulty in collecting this latex due to its rapid coagulation.

The natives allow the latex to coagulate as it flows down the tree and then peel it from the bark. It sometimes runs down onto the ground and is caught in a leaf formed as a receptacle. The result is that the Maniçoba rubber varies a great deal and contains a large amount of foreign matter. When this rubber is properly prepared, however, it is of a very good grade.

The Micandras occurs on the upper Amazon and some are of the opinion that it is used largely in the making of Scrappy Negroheads.

A rubber of the species *Hancornia* is also found in Brazil and is sold under the name of Matto-Grosso Sheets, Mangabeira, or Pernambuco. It is of medium value and rather large quantities of it are used.

The above enumeration does not include all of the varieties of rubber from South America but it does cover the most important ones.

Two Methods of Tapping

All of the South American rubber comes from trees and is obtained by a system of tapping of one kind or other. We shall consider two general methods.

1. Felling of trees.

2. Bleeding by puncture or incision, tapping.

By the felling process it is possible to obtain only the latex which is in the tree at the time of its cutting. The method is a destructive one and is only practiced now under two conditions.

The trees found in Peru, when once tapped are attacked by insects and the death of the tree results, while if this tree is cut down there springs up from its stump several sprouts which grow very rapidly and in a short time a clump of trees exists where there was but one originally. In the second place felling is allowed where it is necessary to thin out the forests in order to make the *estradas*.

Fig. 4—Smoking Caoutchouc

Several different methods of tapping are in use. The *Arrocho* system was one of the first to be used in Brazil, and was accomplished by binding a rope obliquely about the *Hevea,* the knot being high up on the tree. Above the ligature, incisions were made with any sort of tool the operator happened to have, a butcher's knife, pruning hook, or cutlass, and the *seringueiro* cared little whether the incision was too deep and thus impaired the life of the tree, and got injurious material into the latex, or too shallow and thus obtained a poor yield of latex.

From these incisions the latex flows down the tree until it comes to the rope and then on down the groove which the tree forms with the rope until it reaches the lowest point where it is collected in a suitable receptacle. The latex making this journey down the tree collects moss, wooden debris and other impurities and these are all later found in the rubber. In addition to getting poor rubber the *seringueiro* would often neglect to remove the rope and the tree would die of strangulation. This process has been practically abandoned.

Fig. 5—Native Collecting the Latex

The present method of tapping in this region has been described by a great many different writers. Chapel and Carrey have probably given the best description. The *seringueiro* gets his outfit all together which consists of a *machado,* a small hatchet with a short handle and a blade only 3 centimeters wide with a sharp cutting edge of about 5 centimeters, the bucket for carrying the latex, and the *tigelinhas,* small cups which are hung at the different incisions.

With this equipment the *seringueiro* starts out about five o'clock in the morning to operate on his *estrada,* which begins at his hut and after its ramifications leads back to his hut again. He takes with him his *machado* and *tigelinhas.* When he comes to a tree he cleans away the rubbish at its foot, cleans the bark, and then begins to tap the tree. With a single cut of the *machado* he incises the bark, so that the latex flows out, being careful not to wound the tree. After several incisions of this kind have been made in each tree, he places a *tigelinhas* under each one to collect the latex and then moves on and repeats the operation on the next tree.

Some of the collectors make V-shaped incisions and others make vertical ones. Whichever method is used should be practiced regularly on the tree for it has been found that by using irregular tappings the tree will yield regularly only for a year or two and will then dry up and cease to give any latex.

A *seringueiro* is able to operate about fifty trees a day so if his *estrada* contains one hundred and fifty trees he divides it in such a way that each tree is tapped every third day. If his *estrada* contains one hundred, then each tree is tapped every other day. After he has tapped his fifty trees he comes into his hut for a little rest and a cup of coffee.

This has consumed about three hours and he now takes up his *balde,* or tin bucket, and revisits the trees which he has tapped, pouring the latex from each *tigelinhas* into his gathering bucket and turning the *tigelinhas* upside down on a stick near the foot of the tree. This is done to prevent its being filled with water and collecting impurities, as it rains every day during this season of the year.

The period of collecting latex is from the later part of August to the first of January. After all of the latex is gathered he returns to his hut and the remainder of the day is spent preparing the rubber from this run.

Latex is the liquid containing the rubber which exudes from the tree, but is not the sap of the tree. It may be thought of as analogous to the milk of mammals, which it is often called, the rubber corresponding to the butter fat, and of course must be separated out. The process of obtaining the rubber from the latex is called coagulation.

Coagulating Latex

The workman starts a fire in his *fumiero,* a kind of furnace surmounted by a short conical pipe which will deliver the fumes so that they do not spread too far afield. He then fills his *fumiero* with the fuel which has been carefully selected and ignites it. The best fuel for this purpose is the nuts of the *urucuri.* Some wood is mixed with these to keep them burning, and also to conserve the supply.

As soon as the smoke is given off abundantly the *cauchero* takes a paddle and holds this in the smoke from his *fumiero* until it is covered with a layer of carbon. This is done to prevent the rubber from sticking to it. He then dips the paddle into the latex at his side, allows it to drain, then holds it in the dense smoke until it assumes a yellow tinge.

The rubber is coagulated almost immediately and the mother liquor exudes and is evaporated by the heat of the *fumiero.* When this is done, the first layer is complete and he again dips the paddle into the latex and repeats the same process, thus building up a biscuit of rubber with one thin layer upon another and each one coagulated separately.

When this biscuit has attained a weight of ten or eleven pounds he frees it from the paddle by cutting it down in the direction of its axis and is now ready to begin over. These biscuits are still moist and to dry them, he places them in the sun for several days. They are then ready for the market under the name of Para Fine. The size and shape of these biscuits varies considerably in accordance with the way they are made.

The *cauchero* often takes a pole about seven feet long and supports

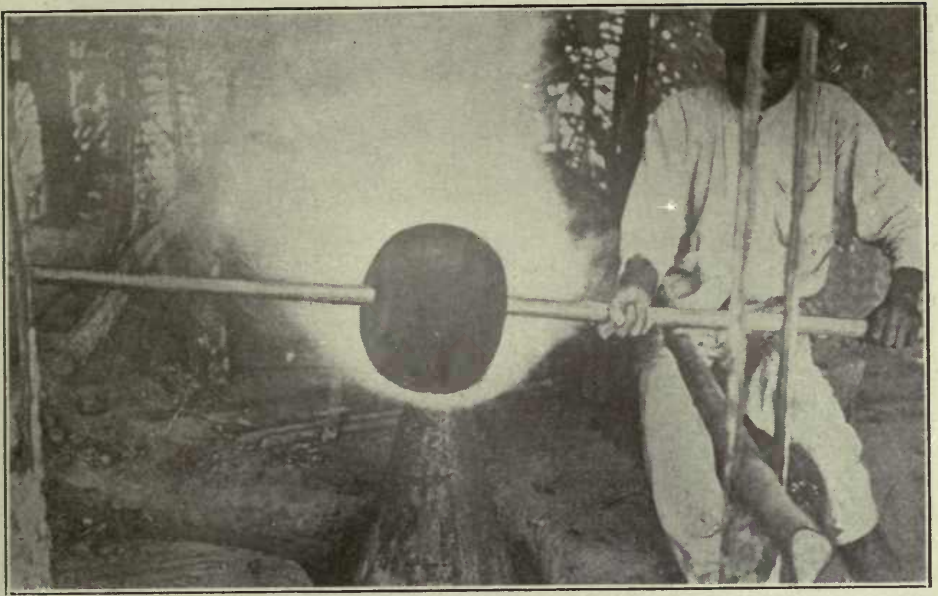


FIG. 6—METHOD OF SMOKING RUBBER

this over his fire by placing one end in a loop suspended from the roof of his hut and holds the other end in his left hand, with which he keeps it turning continually, while with the other hand he pours a small amount of latex over the pole which is in the smoke. By this method the same grade of rubber is produced but in larger biscuits, averaging about forty or fifty pounds. This is the method of coagulating the latex of all of the Paras, and it is undoubtedly the virtues of this process which has given the Para its enviable position in the rubber trade.

There are two reasons at least for the excellence of this rubber; first, the smoke has a large amount of carbon in it and we know this substance possesses energetic antiseptic properties; second, in the products of distillation of the *uricuri* nuts there is a considerable amount of creosote which also possesses the same property. Therefore we have a double protection against fermentation and decomposition of the nitrogenous matter present in rubber coagulated by this method.

The Manihot latex is coagulated by natural heat. As was stated before, the *seringueiro* obtains the Ceará and Maniçoba by tapping the tree with long gashes as high up on the tree as he can reach. The latex is very thick and coagulates before it ever comes to the ground. He allows it to remain two or three days or until it is dry, when he detaches it and either rolls it up into a ball or folds it back and forth upon itself. Without further treatment it comes into the market as Ceara Scraps.

FIG. 7—BALL OF RUBBER AFTER SMOKING

There are three grades of this rubber; the first quality is a blonde rubber which is collected at the beginning of the season; the second quality is darker in color, and is collected later on when the rains have begun to fall; the third quality is that which is collected at the foot of the trees and is full of earthy material, often as much as 50 per cent.

This rubber always gives off a strong smell due to the careless treatment in its collection. Naturally this is a higher grade latex than that from the *Hevea,* and it is a pity that more care is not exercised in its preparation.

A chemical means of coagulation was proposed by Strauss for use with the *Hancornia* latex. It consists in pouring into the latex a solution of potassium alum when coagulation takes place immediately. The rubber is then allowed to drain for about eight days, then divided into small pieces and sun-dried for a month when it is ready for market.

Due to the rapid coagulation, we find enclosed latex all through rubber made by this process which not only constitutes loss but which further ferments and produces a bad odor; we also find pockets filled with the alum solution which has a very injurious effect upon the rubber. As a result this rubber deteriorates with age, and it often has a loss of as high as 60 per cent. There are three grades of Mangabeira, and the one possessing a red color sells at a premium.

This alum process has been displaced in certain regions by sulphuric acid, but this does not remedy the objections already mentioned, and of course it has no antiseptic property. To correct this, a solution of common salt has been used but it leaves too large a quantity of water in the rubber. A soap solution has been used but this, in addition to having the same objections, acts very slowly.

The juices of some plants and climbers have also been employed, but the difficulty of obtaining these and the fact that they introduce more resins into the rubber has resulted in their condemnation.

The above comprise the more important methods of coagulation which are in use or have been used in South America, the best one being the smoking, and it is worthy of mention in this connection that this is the method which de La Condamine found the natives using in 1731.

One thing which consumers of rubber are very anxious to have is uniformity, and there are several factors which tend to produce a poor product:

First, if the trees have been improperly tapped, that is if the *seringueiro* has cut too deeply and pierced the cambium, some of the sap of the tree will enter the latex and impair the rubber, making it tacky;

Second, when in gathering the latex of one species is mixed with that of another or even with that of a tree that is too young;

Third, carelessness in gathering and coagulating. The most uniform varieties therefore are the *Hevea* and *Manihot.*

The following table gives some idea of the relative loss in washing:

Fine Para (hard or soft)	12 to 20 per cent
Negroheads	20 to 40 per cent
Maniçoba	28 to 30 per cent
Matto Grosso	15 to 30 per cent
Mangabeiro	30 to 35 per cent

To give some notion as to the progress made in the production of rubber from South America, the following facts are interesting:

In 1825, less than 30 tons of rubber were exported; in 1830 there were 156 tons; in 1840, 388 tons; in 1850, 1,467 tons; in 1860, 2,670 tons; and in 1897, Brazil alone produced 21,260 tons.

From 1909 to 1913, the yearly average was between 39,000 and 40,000 tons. The May, 1917, issue of the "World's Rubber Position" gives the following estimate of the world's production of rubber in 1916:

Plantation	152,650 tons
Brazilian	36,500 tons
Other sources	12,448 tons

To show the ratio of plantation to Brazilian for several years the following data are significant:

	Plantation Tons	Wild Rubbers Tons
1910	8,200	40.800
1911	14.419	39,730
1912	28,518	42,410
1913	47.618	39.370
1914	71,380	37,000
1915	107.867	37,220
1916	152.650	36.500
1917	223.000	52.628
1918	188.000	40,629
1919	358.000	41.635

CHAPTER III

African Rubbers, Including Those from Madagascar

Varieties

The larger part of the African rubber trees are of the order *Apocynaceae,* of which there are many generae but three of these produce the majority of the rubber. These are *Funtumia, Landolphia,* and *Clitandra.* The rubbers are all more adhesive but less elastic than Para.

Of the *Funtumia* just one species is regarded as of commercial value and that is the *Funtumia elastica.* The gums from the other species seem to be very resinous and the natives are thought to use some of these to adulterate the better gums.

The rubber from *Funtumia elastica* when freshly coagulated has a peculiar sheen to the cut surface and for that reason is sometimes called "Lagos silk rubber." The main varieties of this rubber are what appear in the trade under the names of Gold Coast Lump, Ivory Coast Lump, Niger Niggers, Benin Lump, and some Congo and Cameroon.

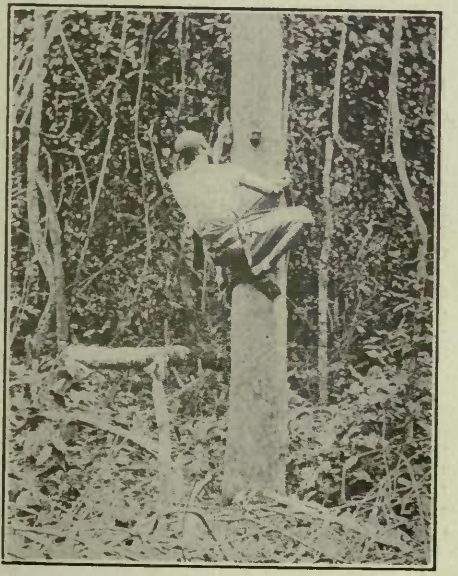


Fig. 7—Tapping Funtumia Tree

The tree grows best in the province of Uganda and the tropical regions of Africa. The tree often attains considerable proportions, in fact trees have been found having a circumference of eighty inches and a height of one hundred feet, a tree as large as the *Hevea.*

This rubber is now being obtained on the plantation scale by several companies in Uganda. As a plantation proposition it has three advantages over *Hevea.* First, it grows more rapidly; second, it yields a larger amount of latex for a small number of tappings; third, it is able to withstand a comparatively long drought.

Fig. 8

The trees recover rather slowly from the wound made by tapping, however. Another great objection is the fact that the tree has so many branches. If planted only a few feet apart it will branch down into the lower regions of the trunk thus producing a dense bushy mass. A tree standing alone branches from the ground to the very top. Of course these branches interfere with tapping and it is found that when they are removed by pruning they heal very slowly and show bad scars for a long time.

Dr. Christy suggested the planting of these trees very closely together and then thinning out later. This has helped considerably.

The tapping of the *Funtumia* is done only two or three times a year, but it is tapped from the ground up to the first branches, generally a distance of fifteen to eighteen feet.

The tapping is of the herring-bone type but must be done very carefully and must also be very shallow. Dr. Christy also suggested that a channel be cut in the bark just deep enough to carry the latex and that the flow be started by means of a pricker.

This method gives about twice as much latex as the Schulz-im-Hofe method, which consists of vertical incisions about four inches apart and extending from the ground up to the branches. It has also been found that if the pricking be done slowly, by beginning at the bottom of the channel and taking several days to complete the real operation of tapping, that a better grade of latex is obtained and also a better yield.

This rubber was first thought to be one of the species *Kickxia* and from the Kew Bulletin of 1890 we notice the following statement:

> "In September, Kew received from Captain Denton, C.M.G., two pieces of the trunk of the Lagos rubber tree, each about ten inches to a foot in diameter, scarred with the marks of the rubber gatherers. They were sent as the 'female' rubber tree, a name, we learn, that is locally applied to the *Kickxia africana*, Benth. It is thus distinguished from *Holarrhena africana*, quite a different plant, which is fancifully called the 'male' rubber tree. The later is also an *Apocynaceous* plant, but not known to yield any rubber.
>
> "Should the new rubber *Kickxia* continue of commercial value, there is no doubt that it will eventually be possible to establish plantations, and thus make the industry a permanent one. It has always been seen that, owing to the climbing habit of the *Landolphia*, which have hitherto yielded African rubber, it was not practicable to cultivate them in regular plantations, as they require the support of other plants, and when once tapped, many years should have to elapse before they would be fit to yield another crop. With the *Kickxia* these practical difficulties disappear. According to Chalot, *Kickxia africana*, has been lately found in Gaboon. Specimens have been measured which were one meter in circumference and twelve to fifteen meters high. Each tree is estimated to yield annually without any injury."

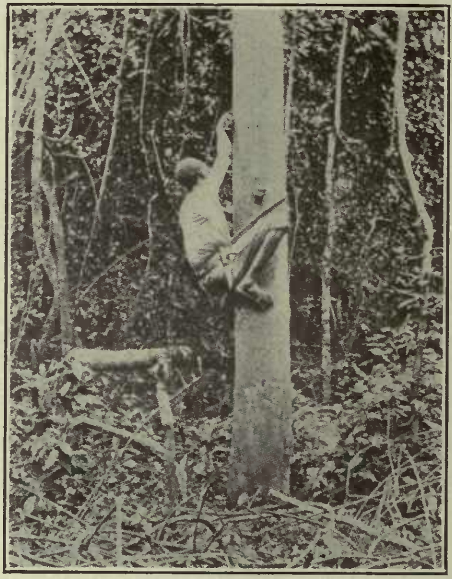


Fig. 9—Swahili Climbing Method

Wright however, in his Cantor Lectures, 1907, points out the error of the Kew observations, for he says:

> "*Funtumia*. This genus has lately become known as a source of rubber in Africa. It is still much confused with the genus *Kickxia*, and it is as well to again point out that Africa does not possess a single species of *Kickxia* of value as a rubber producing plant. The four species of *Kickxia* acknowledged by Stapf. are found only in Java, Celebes, Philippine Islands, and Borneo.
>
> "The genus *Funtumia* is partly African and is represented by three species, *F. elastica*, Stapf., *F. africana*, Stapf., and *F. latifolia*, Stapf. The species of importance in Africa is *F. elastica*, Stapf. Its occurrence has been recorded in Liberia, Gold Coast, Ashanti, Lower Nigeria, Cameroons, Mundame, French Congo, Congo Free States, Uganda.
>
> "The rubber from this species is very valuable, possessing when properly prepared from eighty to ninety per cent of

Fig 10—Tapping a Rubber Vine

caoutchouc. *Funtumia elastica* has been described as a tree with a cylindrical trunk which attains a height of one hundred feet; sometimes the tree occurs more abundantly in local areas, and out of an area of about fifty-four square miles as many as one million seven hundred and sixty trees have been estimated to occur."

The *Manihot Glaziovii* has been introduced into British Central Africa. In regard to the advisability of this project we find a diversity of opinion, some thinking it will prove a fine plantation species and others raising great objections to it.

Before taking up the *Landolphias* it is necessary to define some of the terms which will be used in describing these rubbers.

Ball: The most common form of rubber coming from Africa. These balls vary in size from an inch or less, known as " Small ball," up to four inches or more in diameter, and known as " Large ball."

Thimbles: The natives make these by cutting the rubber up into small cubes, which are sometimes called " Nuts," as for example " Ambriz nuts."

Lump: A very common form of these rubbers consisting simply of large irregular pieces which often become stuck together in transportation.

Flake: A form of lump which is very soft and is used in frictions.

Paste: Practically the same as flake.

Strips: Made from lump rubber by cutting and pressing before it is sold.

Buttons are made in the same manner as strips with the exception that they are in small pieces.

Biscuits and Oysters: The same as buttons.

Niggers and Twist rubbers: A form of ball.

The *Landolphias* are all creepers or vines, yet attain considerable size. Often vines are found having a diamter of six inches. There are several species of importance, the *Landolphia Owariensis, Landolphia Heudelotii, Landolphia Thollonii, Landolphia Sphaerocarpa,* and the *Landolphia Pierrei.* The last two are found largely in Madagascar.

The rubbers from this species referred to in the trade are, Red and Black Kassai from the Congo region; Upper Congo balls and Equateur also from the Congo region; Virgin Sheets and Pinky from Madagascar; Sierra Leone Niggers, Twists, and Cake all coming from the Sierra Leone and southern rivers; Conakry Niggers, Soudan Niggers and Twists, coming from French West Africa; the Bassam Niggers and Twists likewise the Lahou Niggers come from the same territory; Liberia Lump, Hard Flake and Soft produced in the Sierra Leone district; Accra found on the Gold Coast and coming into the market graded as "Prime," " Seconds," " Thirds " and lower grades of " Flake and Paste "; Gaboon, probably the best known Flake; Lapori, a Congo rubber and represented by Balls, Strips, and Cakes, some of the Balls being very clean and good. From Angola we obtain Loanda Thimbles, Niggers, and Prima, also Angola Niggers. There are several grades coming from the port of Mozambique in the form of Marbles, Balls, Spindles, and Sausage.

The *Clitandra* are widely distributed throughout Africa. They, too, are vines and flourish in great numbers on the Gold Coast and the Congo. Their rubber comes into the market largely as Lower Congo in the form of small cubes.

In the above we have not mentioned all of the varieties of rubber which Africa furnishes but we have tried to call attention to the representative classes of rubber now in use.

Coagulation

Concerning the coagulation of these African rubbers not a great deal is known, in fact we do not know how some of them are obtained by the natives. Therefore we shall describe methods in use with the different genera rather than with the different species.

The latex from the *Funtumia* is coagulated by boiling and this is the method employed by the natives. They sometimes use a fusion from the leaves of *Banhinia reticulate* to facilitate the coagulation by heat. This rubber when properly prepared is of a high grade and possesses great strength; for that reason we have the methods used upon the plantations. From the Kew Bulletin we get an idea of the two most general ways:

"There are at present two kinds, namely, 'the cold process' and 'the heat process.' The cold process is chiefly practised by the Fanti men introduced from the Gold Coast. A cavity is excavated in the trunk of a fallen tree so as to form a cistern of the capacity necessary for holding the milk collected during several days. Into this the rubber gatherers pour the milk, after straining it, from day to day until it is quite full. It is then covered with palm leaves and left for twelve to fourteen days, and sometimes much longer, depending on the season, until most of the watery portions have either evaporated or sunk into the wood.

"After being kneaded and pressed together, the rubber thus obtained has a dark brownish color, with the inner portions of a slightly lighter color. Such rubber is known locally as 'silk rubber.'

"The heat process is the one generally adopted by the natives of Lagos. This is much simpler in working, as it disposes of all the milk collected at the close of each day. After being strained the milk is placed in a vessel and boiled. The rubber begins to coagulate almost directly the heat is applied and after the boiling is over is removed in a somewhat sticky condition owing to being burnt, and of a blackish color.

"It is pointed out that the heat process, though simpler, impairs the quality of the rubber, and is calculated to injure the industry. It is probable that if the heat process were somewhat modified the results would not be so injurious.

"An experiment was tried at the Botanic station to coagulate the milk by heat, but not applied directly to it. The result was much more satisfactory. The rubber came off a milky white color, and after being pressed it was clean and firm without being sticky.

"The history of this new rubber industry in Lagos is full of interest, and illustrates the wonderfully rich resources in the vast forests of West Africa. It

FIG. 11—COAGULATION OF LATEX AND PREPARING SHEETS

shows also very clearly how largely these resources can be developed by judicious and intelligent action on the part of the government."

Obtaining and Coagulating Latex from Vines

The methods used by the natives for coagulating the latex from vines are very diverse. The following methods are therefore used on both the *Landolphias* and the *Clitandras:*

It is said that the Red Kassai is obtained by smearing the latex over the body and the natural heat evaporating the water the rubber is stripped off. The collector after tapping the vine collects the latex in his hands and smears it over his body, then proceeds to his hut where he removes the rubber in little bits and makes them into balls. Sometimes after tapping the hand is placed against the incision and the latex flows down the arm and after coagulation this is stripped off like a glove. By either one of these methods the earthy matter is absent but is not absent from the rubbers putrescible matter.

The Black Kassai is obtained by a process of boiling and smoking.

The " Ball " rubbers are obtained by bruising the vine. In some localities as the latex exudes, some salt solution is poured over it by means of a shell. This coagulates the latex and a little lump of rubber is drawn off, and by keeping the bruised place moistened with the brine the rubber is drawn into a thread which is wound around and around the original lump as a nucleus.

Very often the natives will start five or six such places and then retreat a few steps and wind all of these threads into one ball of convenient size to hold in the hands. They make large balls of rubber in this same manner by taking the ball when it has become too large to wind in the hands, and lying on their backs, supporting it on the stomach and continuing to wind it with the hands. The salt solution as we know is a good antiseptic and therefore this rubber does not as a rule develop foul odors, but it does contain large amounts of occluded water and brine which are objectionable.

Perhaps the most common way of obtaining the latex from vines consists in cutting them down and bleeding or allowing the vine to dry out and then removing the rubber by a process of maceration.

The method mentioned above of

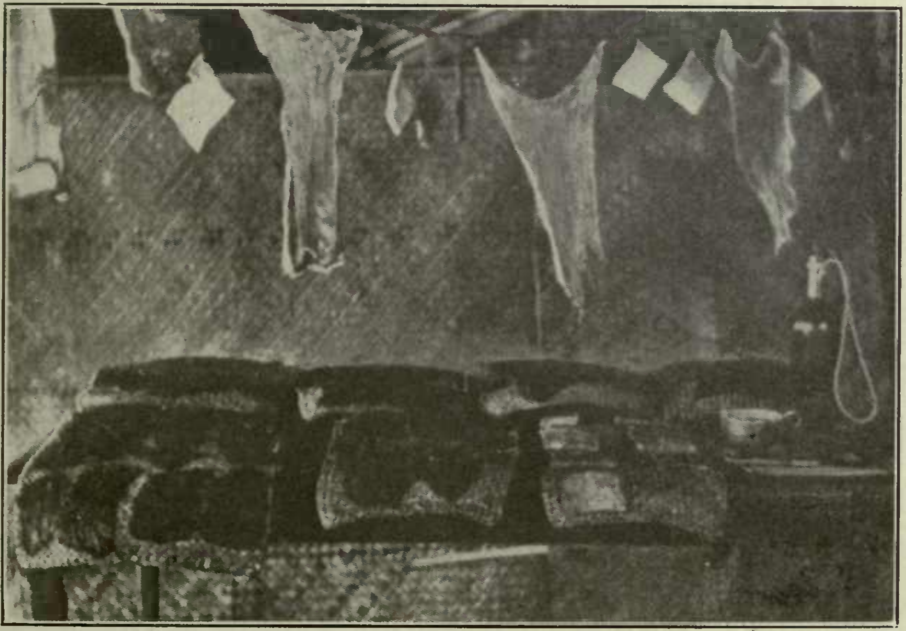


FIG. 12—DRYING THE SHEETS OF RUBBER

cutting down the vines and creepers which produce rubber and then bleeding them is very wasteful for a large part always remains in the wood. To overcome this the Madagascar Rubber Company, Ltd., has put into operation the following method:

They cut down the vines and creepers and allow them to dry when the rubber which they contain rapidly coagulates. The dried material is now fed into a machine which grinds it to a pulp in the presence of water. After leaving this machine it goes through several machines called "agglomerators" which bring the particles of rubber together and at the same time wash away the wood fibers. This process has effected quite a saving in rubber.

Another method of coagulation by natural heat employed by the natives consists in tapping, after cleaning away the debris from the ground. They then allow the latex to collect in the sand which removes part of the water by filtration, the remainder being evaporated by the heat of the sun. The native returns later and gathers up the lump of rubber with all the foreign matter which adheres to it and then delivers it to the buyer. This method is very much preferred by the natives for it requires about the least amount of labor of any method known to them.

The rubber obtained by this careless method not only contains the foreign matter which it naturally picks up and which the native purposely adds, but also pockets of occluded latex containing nitrogenous matter which putrefies and not only injures the rubber, but gives it a nauseous smell. This method is used largely in West Africa and to some extent in the Congo and Angola.

A method also used in the Congo consists in tapping the vine in several places, one below the other. At the lowest one the native fixes a leaf in the form of a trough which will conduct the thin stream of latex out into a collecting receptacle. The leaf is generally made secure either by means of clay or partly coagulated rubber. The collecting receptacle has a hole in the bottom which is carefully corked up. When the latex has ceased to flow there is added to it four or five times its volume of water and it is allowed to stand. The rubber then comes to the top in the form of a semi-solid cream.

The native then removes the cork from the orifice in the bottom of the

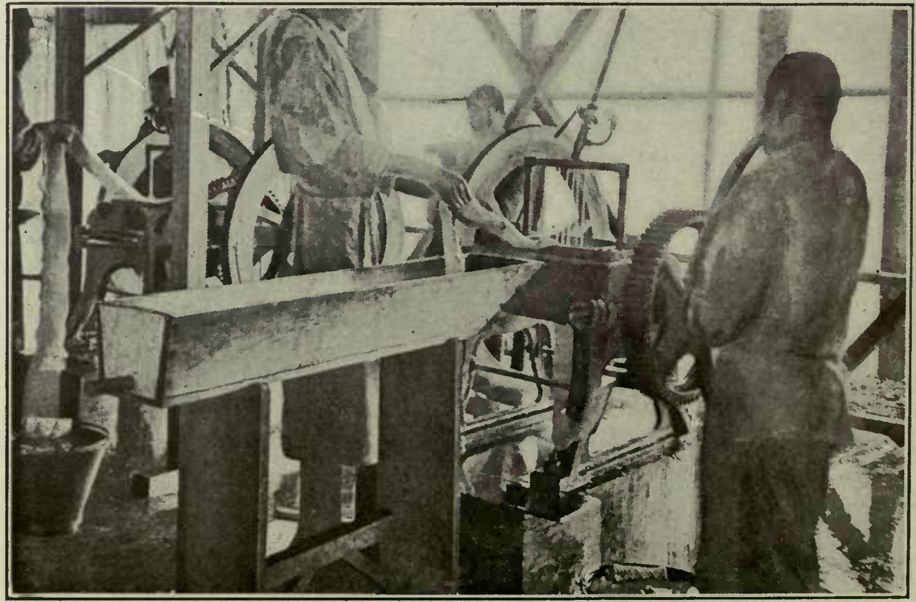


Fig. 13—Preparing of Funtumia Rubber

container and draws off the lower liquid. This contains the majority of the putrescible matter. The rubber is then removed to wooden containers where it is exposed to the air for some time, depending upon its condition. The native judges from its appearance when it is ready for kneading. If it gets too hard for this it is cut up into small parts and is sold as " thimbles."

This method is open to the same criticism as the others; namely, the putrescible matter is enclosed in pockets where it decomposes and produces a sickening smell.

The process of using potassium alum is in vogue in Africa in just about the same manner as in South America.

Citric acid has been used with the latex from the *Landolphias* but it has been completely replaced by sulphuric acid in Madagascar. Lime juice has also been used in a few localities. These all have the same objection that they coagulate too rapidly and thus enclose some of the latex.

The properties of these African rubbers may be summarized as follows: Gold Coast Lump, from which Strips and Buttons are made, is a very good grade of rubber. The Flake, however, is generally wet and has a bad odor. Ivory Coast is also a good rubber. Niger Niggers at first were very poor, suffering a loss as high as forty to fifty per cent upon washing, but they are coming into better repute at present.

Benin is generally very dirty and has a very bad smell. Congo contains bark and water, likewise pocketed latex. The Red Kassai is the best rubber from Congo possessing a high tensile strength. The black is not as good and does not come as clean.

The Sierra Leone comes in several grades containing bark and grit but low in moisture. Equateur is a much esteemed rubber. Bassam Niggers if in the form of small balls are good. Lahou Niggers are about the same. Liberia is wet and a more or less pasty rubber. Accra varieties are of a fair rank.

Gaboon is coagulated by an unknown process. It is very bulky but will take the form of the container in which it is shipped. It runs very high in moisture. The Lapori is a variable rubber as some of it runs in good clean condition and some contains fermented milk.

The Loanda is gradually disappearing and its place is taken by Angola Niggerheads. The Mozambique rubbers are sold largely in the Liverpool market where they are in demand. The Pinky from Madagascar is a very good rubber, but, due to the reckless methods of obtaining it, is liable to become extinct.

From the following table showing the loss in washing one may obtain an idea of the relative values of these African rubbers.

Red and Black Kassai and Equateur, 6 to 12 per cent; African Niggers (Soudan, Conakry, Sierra Leona, Niger), 15 to 40 per cent; Madagascar Pinky, 18 to 20 per cent; Madagascar Niggers, 40 to 50 per cent.

CHAPTER IV

Central American Rubbers

When we refer to the rubber from Central America we generally include the territory where we find the Castilloas growing. This includes, therefore, not only Central America proper, but also Colombia, Ecuador and Venezuela, in fact, territory north of the Amazon including Mexico. In a previous chapter we mentioned certain rubbers from Ecuador and Colombia, but now we shall call attention simply to the rubber obtained from the Castilloas.

The rubber balls used by the natives in the game which Columbus and the early exploiters found them playing was of the Castilloa variety.

Varieties

This rubber tree found native in Central America and Mexico is called *Castilloa lactiflua,* in honor of Castillo, a Spanish botanist who died in 1793 while preparing the flora of Mexico. *Lactiflua* means flowing milk, distinguishing it from other trees from which the milk exudes but does not flow freely. The tree generally is called *Castilloa elastica.* It is a significant fact that at one time there was more Central American rubber used in the United States than there was of Para. It does not possess the strength, toughness or elasticity of Para.

Fig. 14—Mexican Rubber Gatherer

Fig. 15—Tapping Castilloa

The varieties of rubber from this region which are more or less familiar to the trade are Guayaquil sheet, coming from Ecuador and Colombia;

there is also some Guayaquil and Carthagena strip, some in the form of sausage, and some designated as No. 1 and No. 2; their production is on the decrease at present.

A grade referred to as Mexico comes from Vera Cruz, Tabasco and Baraca. Guatemala furnishes a rubber bearing the same name. These rubbers are rather inferior in quality. It is thought that they are mixed up with cheap molasses, as some are very tacky.

Nicaragua sheets and several grades called West Indies, which never furnish any rubber, along with Nicaragua scrap are familiar rubbers from this territory. The Nicaragua rubber is generally quite dry but rather dirty. The Greytown scrap is considered about the best rubber from this district.

In order to encourage the production of rubber the government of Nicaragua gives a premium of ten cents for every rubber tree planted where the number does not go below two hundred and fifty planted for each person. The trees must be planted sixteen feet apart.

Virgin or Virgen comes in the form of strip and sheet and slab. It is obtained from a different tree than the others mentioned above and is used to a great extent in the manufacture of hard rubber.

Guayule is a rubber from this section unique in its growth and production.

The above comprise the rubbers which we shall consider in this article. The better grades of Centrals shrink from 25 to 30 per cent. and the remainder from 30 to 40 per cent.

The method of obtaining the latex in use in Central America consists in puncturing rather than tapping, the tree being punctured higher up than is the custom in the case of any other species we have considered.

In order to coagulate the latex the native uses some very primitive means. For instance, he sometimes adds to the latex the juice of the " amole " vine. Often this is carried out in a hole in the ground. One pint of amole juice, which is alkaline in reaction, is added to one and a half gallons of latex. In a more modern way, after adding the juice the whole mass is heated to between 165 deg. and 175 deg. Fahr. By this method they are able to obtain sheet. The part which dries on the tree and is peeled off is called scrap.

FIG. 16—COAGULATING WITH VINE JUICE

The *Coyuntla* juice is an astringent in nature which will coagulate the rubber if the weed which contains it is used to whip the latex.

The natives in some places pour the milk from the tree onto mats, where it is allowed to dry or evaporate, then when the rubber is separated from the mat a sheet results. Several of these sheets are pressed together and are then ready for market.

Another method similar to the last consists in pouring the latex out onto the long, palm-shaped leaves of the *Oja blanca* which they have dried in the sun.

When the leaves have a coating of about a quarter of an inch they are piled one above the other and pressed to remove moisture. The strips are then separated from the leaves, packed into slabs and are ready to be transported.

A very common method of coagulation in Central America is doubling the volume of the latex with water, then allowing it to stand. In a short time the rubber comes to the top in a creamy consistency. When homogenous enough it is removed, and in some localities is placed in the sun to dry, while in others it is run through between wooden rolls which press out the excess water. It is then placed in the sun for about fifteen days to dry still further. This rubber suffers a loss of as much as 50 per cent, as it contains so much occluded water and uncoagulated latex.

All of these rubbers as prepared by the natives are not of the quality which they might be if more care was exercised in their production

Rubber is now being produced from the Castilloa on a plantation scale at different places. To get an idea of these plantations, we shall describe the industry as we find it in operation by the La Zacualpa Rubber Plantation Co.

The development of the industry in Mexico is told in a little book. "Rubber, What It Is and How It Grows," published by the above company. In describing this rubber business we shall therefore use extracts from this work.

The lands in Mexico suitable for the production of this rubber are located in the states of Vera Cruz, Tabasco, and Chiapas, for the elevation above sea level should not exceed five hundred feet. The low lands along the coast are the best, where the soil has a great depth formed by the deposits left by the overflowing rivers.

Land for a plantation is generally selected which has a virgin forest rather than land which has been under cultivation. It must be capable of perfect drainage and yet protected from overflowing rivers. In the above mentioned plantation there are over ten thousand acres of trees, averaging about four hundred trees to the acre. These trees attain a height of from forty to fifty feet and a diameter of about twenty inches.

The Castilloa begins to blossom

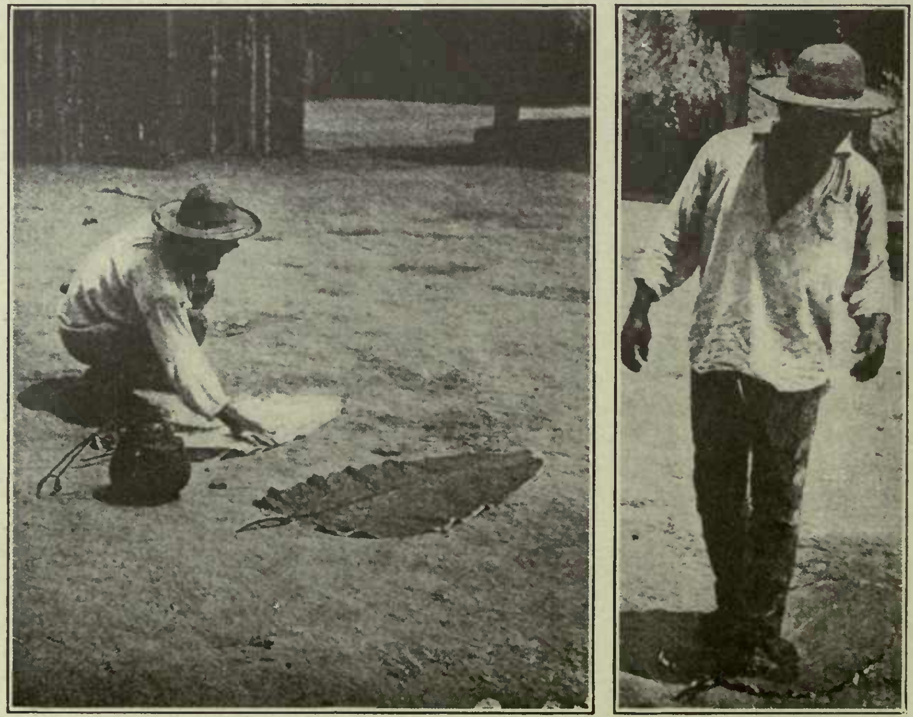


Fig. 17—Preparing Rubber on Oja Blanca Leaves

Spreading Latex on Leaf Pressing Out Moisture

Fig. 19—Preparing Rubber on Oja Blanca Leaves
Removing Rubber Sheet The Finished Sheet

when it is between five and six years old. Before blooming it sheds all of its leaves, this taking place between January and April. When the seed is ripened the tree puts forth new leaves.

The planting of these trees is very interesting. The land is first surveyed into tracts of thirty-three acres, including avenues and streets; the roads running north and south are called avenues and are named, while the ones running east and west are called streets and are numbered.

The land is cleared by cutting down the forest, and is then burnt over. It is then staked out to allow four hundred trees to the acre, and at each stake a mound of earth is made and the rubber seed planted, which germinates in from eight to fifteen days and grows quite rapidly.

After planting, a great amount of work is required to keep the natural vegetation from choking out these tender trees. After about two years the tree requires very little attention. The tapping begins when the tree is between five and six years old.

The old method consisted in making a V-shaped incision in the tree and placing a leaf under this to serve as a funnel and conduct the milk into a hole in the ground made at the foot of the tree. This hole was lined with green leaves. In a short time the latex coagulates on the edges of the incision and stops the flow. This is removed as often as necessary until the milk ceases to run.

To tap twelve trees and obtain their full quota of latex is regarded as a day's work for one laborer. When the flow has stopped the tapper carefully removes the leaves containing the latex from the hole and pours it into his gathering receptacle. It is a very wasteful method at best. When some of these trees are first tapped the milk will spurt out some distance, just as though it were under pressure in the tree.

The new method of tapping we shall take from the book referred to above.

"The hulero, or rubber gatherer, is supplied with a tool invented and perfected on La Zacualpa Plantation, consisting of a stout handle, twelve inches long, at one end of which a U-shaped sheet of steel is fastened; just forward of this U, the curved portion of which is sharpened to a keen edge, a metal finger is depressed more or less as desired by an adjustable screw which runs through the handle; and the 'set' or 'adjustment' of this finger, which slides over the surface of the bark as the tool is drawn across the tree, determines the depth of the cut made by the U-shaped knife which follows immediately behind the metal finger.

"A deeper or shallower cut may be made according to the size of the tree which we are tapping and the thickness of the bark; and we can effectually guard against cutting through the bark and into the wood of the tree. The latex, or rubber-producing milk, flows in veins in the bark only, and is entirely distinct from the life sap of the tree which flows between the bark and the wood. It is impossible to avoid cutting into the wood when the machete is used, and it is from the machete's too deep cutting that injury to the tree results.

"With our perfected tapping tool a smooth continuous channel is cut across the tree's trunk and a canal is made which cannot fail to conduct the latex to a receptacle placed to receive it; while the succession of hackings made by the machete are often out of line and much of the latex flowing along the cuts leaves the line of travel and is lost."

The method of treating the latex on the plantation is quite different from the wasteful and dirty ways of the natives. The exact process of coagulation is kept secret, but after it is coagulated the rubber is washed through a modern washer, sheeted and hung up to dry, then by means of a hydraulic press these sheets are made into solid blocks of about twenty-five pounds each, when the process is complete.

In Mexico a shrub is found which produces rubber and is not known to grow in any other locality. A careful study of this plant has been made by Francis Ernest Lloyd, Professor of Plant Physiology, Alabama Polytechnic Institute, and from his account we get a good idea of this particular rubber plant. It bears the name Guayule (*Parthenium argentatum*) and flourishes on the Chihuahuan Desert.

It was discovered by J. M. Bigelow in 1852, while attached to the Mexican Boundary Survey, and was first described by Prof. Asa rubber was first obtained from it by the natives by chewing the bark and then collecting the rubber together in a ball.

This method of getting the rubber

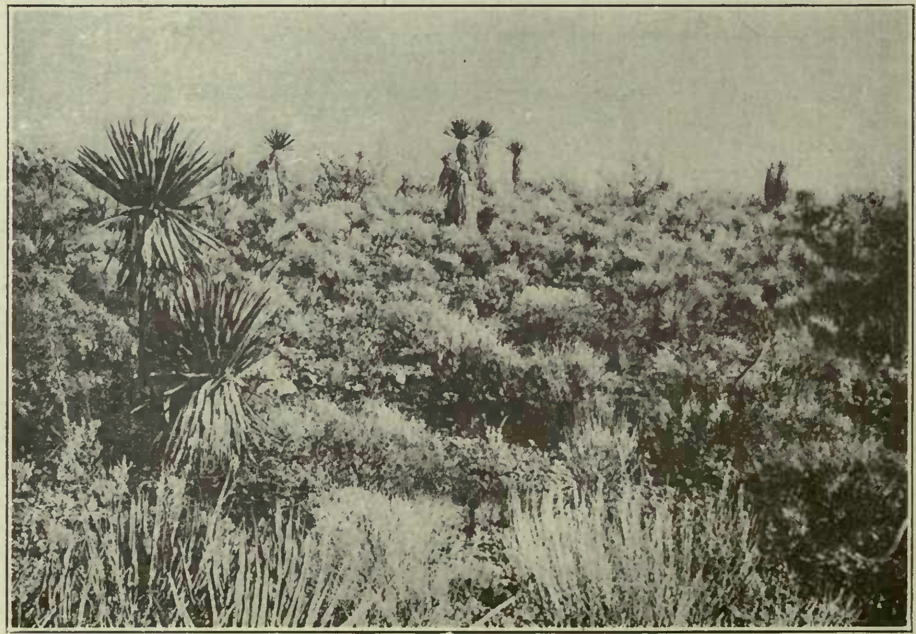


Fig. 20—Dense Growth of Guayule

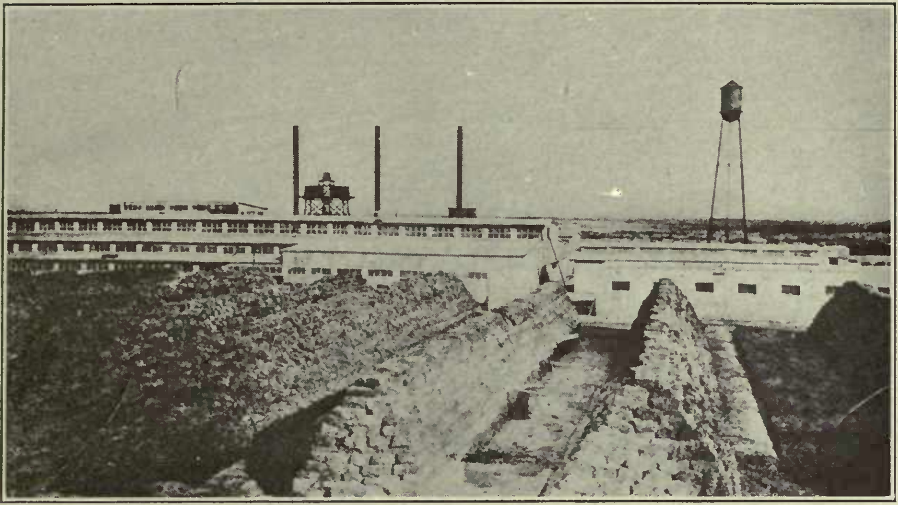


Fig. 20—A Guayule Extracting Factory

dates back a great many years. To substantiate this belief Professor R. H. Forbes furnished the following information:

> "The lump of rubber, a portion of which I recently handed you, was found in December (or thereabouts), 1909, at the west end of the Santa Cruz Reservoir and Land Company's dam, 14 miles west of Sasco, Ariz. C. O. Austin, who was present, states that this ball of rubber was contained in a small *olla* with articles of stone belonging to the older prehistoric ruins of the country.
>
> "The find was made at about three feet below the general surface which was formed by the off-wash of an adjacent low mountain. No traces of houses on the present level of the land, according to Mr. Austin, were visible. One other ball of rubber was found here, and is now in Col. W. C. Greene's collection at Cananea. I regard this find as genuine, as Mr. Austin is familiar with Salt River Valley ruins and his statements are confirmed by others."

Because of the resinous content of this plant it burns rapidly, and large quantities of it have been used in Mexico as fuel in smelting.

About the first move to utilize this rubber was in 1888, when a company sent an agent into Mexico with instructions to obtain some of this "rubber bark." He carried out his orders carefully and had shipped to New York 100,000 lb. of the entire shrub. The freight on this large amount of wood so discouraged this company that further efforts to obtain this rubber were not undertaken immediately.

In 1902 a factory was built at Jimulco for the extraction of this rubber. A little later a large factory was built at Torreon by the Continental-Mexican Rubber Co. Since this several large factories have been built for extracting the rubber out of the shrub.

The methods used for extraction of this rubber are interesting, for they are different from any mentioned thus far; something like it was outlined in connection with the Landolphias, however.

The methods differ because the rubber which the plant contains cannot be removed by bleeding, for it exists as rubber in the cells of the plant itself. There are two general methods which have been and are being used. The first consists in dissolving the rubber by means of chemicals after the shrub has been subjected to preliminary grinding.

The other method consists in agglomerating the rubber mechanically after it has gone through the preliminary grinding. This method has just about been abandoned, as it is impossible for it to compete with the mechanical method. The first process consists in extracting the rubber from the ground shrub by means of naphtha. The resulting solution is then

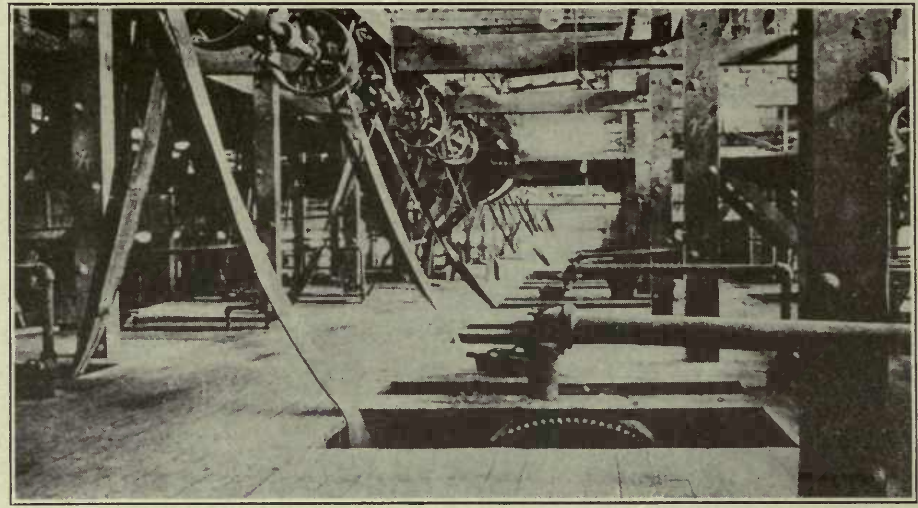


FIG. 21—UPPER FLOOR IN GUAYULE FACTORY

partly distilled, after which alkali is added. This holds the resins in solution and the rubber separates out.

In the other method the shrub is pulled up root and all and brought to the store houses for a short period of seasoning, as it seems to work better after such treatment. In the more improved process instead of pulling up the shrub it is cut off at the ground, and this allows it to send up sprouts, which in time will produce rubber.

From the store houses it is taken and washed to remove dust and sand which would adhere to the rubber and increase its specific gravity. It is then passed between corrugated rolls, running differentially, which cut the shrub and grind it at the same time.

The mass is then passed into a pebble mill, the charge generally consisting of one-third its volume of pebbles, one-half of water, and from six to eight bushels of shrub. The mill rotates at the rate of thirty revolutions to the minute for from ninety minutes to two hours, when there results a fine pulp mixed with little particles of rubber.

This is separated as well as possi-

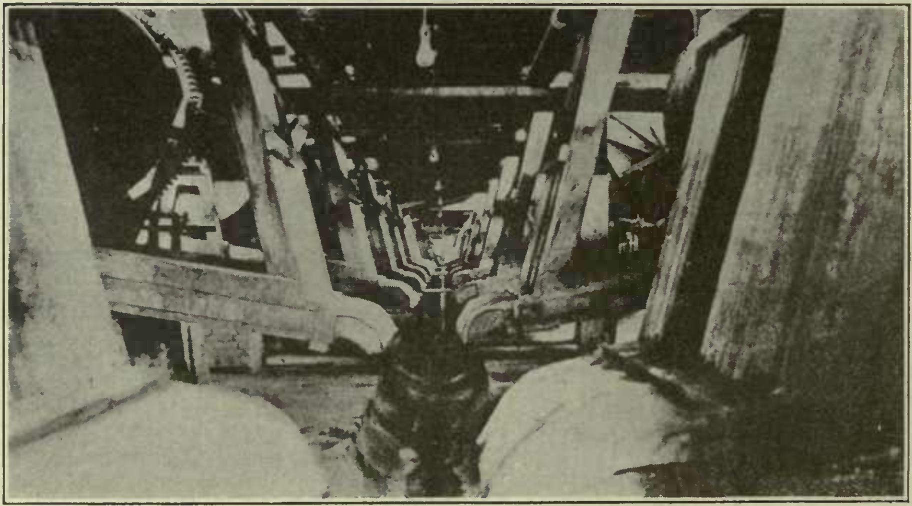


FIG. 22—TROUGHS TO COLLECT EXTRACT FROM PLANTS

ble from the dirty water which it contains and then transferred to settling tanks. The rubber then comes to the top and is removed by skimming, thus separating it from most of the fiber, which water-logs and sinks. To clean the rubber still further it is often put through a beater-washer and scrubbed for some time, when it goes between corrugated rolls again and scrubbed for some time, when it sheet it and make it ready for the market. This rubber contains about 25 per cent of moisture.

In some places they take this rubber just as it comes from the settling tanks and boil it with a 1 or 2 per cent. solution of caustic soda, which will separate the rubber more completely from the fiber, and will also reduce the per cent. of resin which normally runs about 25 per cent. The resin has also been removed by extracting the Guayule with hot acetone.

According to Weber, the Centrals suffer the following commercial losses:

	Per cent.
Guayaquil (sheet)	20 to 30
Guayaquil, Carthagena (strip)	20 to 30
Mexico	12 to 15
Guatemala	25 to 35
Nicaragua (sheet)	10 to 15
Nicaragua (scrap)	10 to 15
Virgin sheets	12 to 15
Guayule	30

CHAPTER V

Rubber Plantations and Their Development

When we consider plantation rubber our attention and thought are directed to that produced in Ceylon, the Federated Malay States, Dutch East Indies, Borneo, and the Pacific Islands. In this chapter we shall consider the establishment and maintenance of the rubber business in these areas.

The tree which is now almost exclusively planted upon these plantations, and thus furnishes the rubber, is the *Hevea,* the descendant of the tree which was first found in South America.

It was Herbert Wright who in 1834 suggested that it would be profitable to plant some of the best species of rubber producing trees in the East and West Indies, for even at this time Hancock, who was experimenting with rubber, was having difficulty in obtaining the crude rubber.

The real plantation industry as we know it, however, dates from the work of Sir Joseph Hooker, director of the Royal Gardens at Kew, Sir Clements Markham, connected with the India Office, and Collins, Cross and Wickman, who made excursions collecting material.

In 1873 Collins obtained some seeds of the *Hevea* from the Amazon region and took them to Kew. In 1875 he collected some from the *Castilloa* and after many trials and hardships succeeded in landing these at Kew. In 1877 he obtained more seeds from the *Hevea* and no doubt some of the trees in the East to-day are direct descendants from these seeds.

In 1876 H. A. Wickman, who was living in the rubber region of the Amazon, was commissioned by the Indian Government to obtain a supply of *Hevea* seeds. The Government of Brazil was opposed to the shipping of these out of the country.

Wickman fortunately had the opportunity to charter a large steamer which had given up her cargo and was about to return empty. This he did and with the aid of all the laborers he was able to get he started out to collect the seeds. They succeeded in obtaining the supply and the cargo was passed as one of "botanical specimens." It contained many thousand seeds. These were also taken to Kew, and when planted only about four per cent germinated.

Although the Indian Government financed the undertaking they selected Ceylon as the proper place to carry out the experiment. The principal nursery for trees in Ceylon was located at Henaratgoda. Dr. Trimen was in charge of the gardens and in 1881 the first flowers were seen upon these trees.

In 1884 there were over one thousand trees there but in 1885 the number was considerably reduced owing to the necessity of thinning out.

In 1893 over ninety thousand seeds were distributed to planters in Ceylon, Malaya and elsewhere.

Trimen made the first experiments on tapping planted rubber trees in 1888 and came to the conclusion that a big profit could be realized.

To show how the industry has grown the following figures might be interesting:

Ceylon

In 1890 about 300 acres had been planted; in 1900 about 1,750 acres; in 1904 about 11,000 acres; in 1906 about 100,000 acres, which in 1912 was increased to 230,000 acres and in 1913 showed an acreage of 235,000; at present 250,000 acres have been planted.

FIG. 23—HEVEA SEEDLINGS READY FOR PLANTING

Malaya

In 1897 about 350 acres had been planted; in 1906 about 100.000 acres were under cultivation; in 1912 about 620,000 acres had been planted. This showed a further increase in 1913 to 667,000, and is still growing.

Notice how rapidly the industry developed in Malaya.

In Java there are probably about 150,000 acres planted, and in Sumatra about 70,000 acres.

A table showing the production of rubber from Ceylon and Malaya is interesting:

YEAR.	CEYLON EXPORTS.	MALAYA EXPORTS.
	Tons.	*Tons.*
1906	147	425
1907	248	1,036
1908	407	1.665
1909	666	3,340
1910	1,472	6.500
1911	2.900	11.000
1912	6,697	18.956
1914	15,335	50,404
1915	21,785	79.415
1916	24,334	111,394
1917	32.289	153.024
1918	21.080	140.659
1919	37.351	240,109

This gives some idea of the great business which has grown up so quickly.

Now we will trace more in detail how these large plantations have been established.

The *Hevea* was found to grow in a belt which is included within ten degrees of the Equator, provided there was plenty of moisture. Although it flourishes best on the lowlands, it is found giving good returns at an elevation of twenty-five hundred feet. It will grow in comparatively dry districts if it is protected from the wind, but of course the growth is slower and a longer period of time is taken before it is ready to produce any rubber.

As a general rule, we might say that rubber could be produced on almost any soil in the latitude of Ceylon up to an elevation of two thousand feet, provided the soil receives at least seventy-five inches of rainfall a year. It is found that *Hevea* does best upon soil where virgin forests have been removed.

Planting Rubber Trees

Before planting, therefore, a great amount of work must be done to clear the land. This is done by cutting down the trees and underbrush and then burning it over when it is dry. In some localities, the stumps are removed by means of dynamite. It is found best to remove all dead wood and not allow it to rot upon the ground, for that removes the increased danger of the young trees being attacked by white ants and root diseases. After this land is cleared, it requires a vast amount of labor to keep down the weeds which immediately spring up.

Large nurseries must be established to supply the plantations with plants which must be at least a year old when set out. The selection of the site for the nursery is an important matter. It must be close to the fields where the plants will be used and it must be in rich soil with plenty of moisture and protected from the winds. It is not always an easy matter to find such a site.

When planting the seeds, plenty of room must be allowed for the plant to grow. Generally seeds are placed at a distance of no less than six by six inches. Several times the actual number of plants needed should be raised so that only the best may be used. That is the great disadvantage in the method of planting seeds at stake where the plant remains whether good or bad.

In the Malay States they often plant the seeds in individual baskets which are later taken to the plantation with the seedlings and planted without disturbing the plant in the least. This has the same objection as the method of planting at the stake.

The same area should never be used over as a nursery unless it has been thoroughly dug up, limed and then allowed to remain fallow for some time. This is done to destroy all the insect pests.

Planters have learned to realize that great care should be exercised in selecting the seed. When a breeder of cattle is desirous of producing beef cattle he selects the largest of his cattle to produce this strain, and, by continued selection, he arrives at the desired result. If, on the other hand, he wishes to build up a fine dairy he selects the ones from which he gets the largest amount of milk, and, by continued selection of this sort, arrives at a different result. So it should be in the selection of seed to produce the rubber plantation.

In the past the planters have striven to obtain their seeds from the oldest trees regardless of whether they produced much latex or not, and it has been found that trees will vary as much in their yield of latex as cows will in their production of milk. It is, therefore, best to collect the seed from the trees which produce the most latex, everything else being equal.

It is not an easy task on a large plantation to pick out a tree here and

Fig. 24—Weeding Young Rubber

there and then collect seed from these trees only. So it has been recommended that certain areas of a plantation be set aside for producing the seed for future plantations; that these trees all be tapped in the same manner and at the same time and the yield of each tree carefully kept.

After ascertaining which are the best trees the others are cut down and their stumps are drawn out. When the time for producing seed arrives the tapping is stopped and the seed allowed to develop and is then collected. In this way only seed from the best yielding tree will be used and thus future plantations should produce more rubber than the present ones, which have been propagated from seeds taken from the oldest trees regardless of yield.

As to drainage there are two distinct kinds. In the Malay States the rubber is planted on the low alluvial deposits where the water level is only a foot or two below the surface of the soil; while in parts of Ceylon and other territories the trees are planted upon steep hillsides.

In the first case the water must be removed to a river or the sea, and this is effected by a system of canals cut through the plantations. This work sometimes is done by the government before the land is leased or sold for plantation purposes, but generally it must be done by the promoters themselves. In some localities the canals must be very frequent, in fact between the rows of trees, and the trees are really planted upon the earth thrown out in the digging of the canals.

In the second system drains are not cut so that the water will be removed, for the natural slope will take care of that, but in such a way that the water will be removed so as not to wash away the soil so rapidly. To do this small ditches are cut across the slopes with a gentle fall and are carried along until they enter a natural ravine. The number of such drains is dependent upon the slope of the land; of course the steeper the slope the shorter the distance between them.

Irrigation has been little practiced as the few attempts thus far made have been failures.

The number of trees to the acre has been a much debated question, some contending that best returns are obtained from three hundred trees to the acre and others claiming as low as fifty, and between these limits we find every conceivable number recommended.

If the trees are planted 12 by 12 feet apart we find three hundred to the acre; if 30 by 30 feet apart then fifty to the acre. If the trees are planted close together, during their early years of tapping they are not crowded and of course more trees are producing, but as they get older and do become crowded, then their yield when it should have increased will be found to decrease and the advantage is in favor of the trees farther apart. It is generally thought at this time that 150 trees to the acre give the best results, though we have not had enough experimental data along this line as yet.

The planting is done in holes about a foot and a half deep at least, the larger the hole the better. In some places the holes are made and the ground loosened by the use of dynamite.

When planting, the ground is tamped in tightly around the seedling and in some places they are stumped, that is the whole top is cut away leaving just a stump. The roots are also cut off short and the tap root is severed. This planting is done during the rainy season, and even then the young trees are mulched to protect them in case of drought.

The trees grow very rapidly. In Ceylon a *Hevea* will grow from six to nine feet a year during the first few years and its girth will increase at the rate of three or four inches a year. The greatest growth takes place after the third year until the branches become very thick; then it grows more slowly.

In the Malay States the growth is more rapid and a four years' growth there is equivalent to a five years' growth in Ceylon. Some trees in Ceylon that are about thirty-six

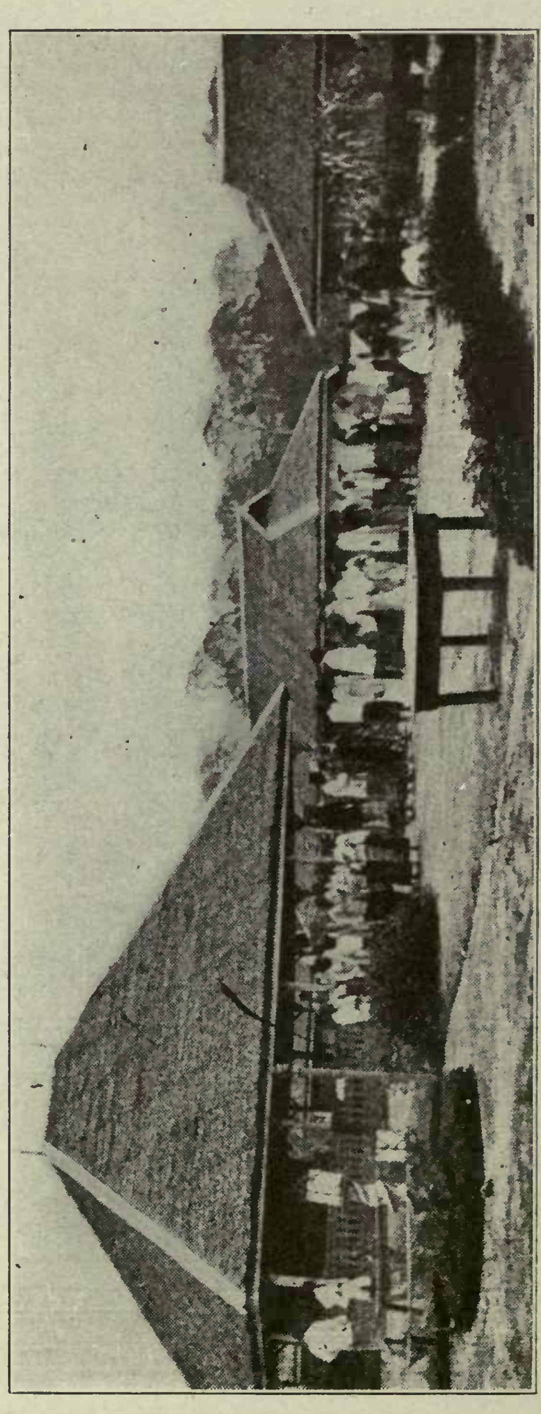


Fig. 25—The Coolie Quarters

years old have attained a height of eighty-five feet.

Cultivating the Land

The weeding which follows the planting is a vexing problem to the planter. A great deal of it of necessity must be done by hand. Some harrows drawn by oxen are used but the systems of drainage and unevenness of the ground makes it almost impossible to use any of the modern machines which recommend themselves for such work. Therefore large numbers of coolies are employed to remove the weeds.

As soon as the job is completed once they must turn right around and go over it again, for it becomes a very expensive operation if the weeds once get the start of the weeders. It is necessary to remove the weeds not only because they choke the young seedlings but in case of a drought they rob the trees of the moisture which is imperative for their growth.

While the trees are young and of course non-productive it has been suggested that some other smaller crop be grown between the trees. This practice is called "intercropping." Tea has been raised and also coffee. Indigo has been recommended and at first thought seems reasonable as it is a leguminous plant and thus collects nitrogen from the air. But the synthetic indigo has driven the natural product out of the market.

Many are of the opinion, however, that intercropping is a bad practice, as it checks the growth of the trees and what is gained from the intercrop is lost when it comes to the main industry, the production of rubber. When an intercrop is cultivated and then dies as a result of the trees' shade it must all be cleared away so that it does not furnish a center for the development of fungus diseases.

The use of artificial fertilizers is believed to be advantageous. Potash has been found to produce a better growth in the tree and also seems to help the renewal of bark where it has been removed in tapping.

Too much nitrogen is a bad thing as it tends to make the trees brittle and also top-heavy. Nitrogen is necessary for plant growth and is the most expensive to supply to the soil in commercial fertilizers. To obtain nitrogen in soils which have become depleted, therefore, they resort to what is known as "green manuring." Leguminous plants are sowed broadcast over the freshly cultivated ground. These plants as they grow take up nitrogen from the air and make it available for plant use. These plants must be cut at the proper stage, however, generally at intervals of from four to five months.

As the trees grow larger there comes the question of pruning and thinning. Very little pruning is done other than to remove the dead branches or ones that are found low down on the trunks of the trees which have been planted far apart.

Thinning presents a serious problem. Just what trees shall be removed? Of course, the weakest ones or those diseased should be cut down, but this often breaks up the regularity in the spacing of the trees. A careful record of each tree should be kept and those yielding the largest amount of latex should always be kept, regardless of position in the plantation. Here again all signs of the removed trees must be destroyed.

Tapping the Trees

At the age of from four to six years the trees have become large enough to be tapped and begin to yield a small return. At this age the workers go through the plantation and measure the trees to ascertain what ones are suitable for tapping. Any tree which has a girth of eighteen inches three feet above the ground is marked for tapping. Trees of this size have bark thick enough so that it will renew and the tapping will not permanently injure the tree.

After the trees are selected for tapping the operation becomes purely a routine one. The laborer starts out early in the morning and taps the trees allotted to him, at this time placing the little cups in position to collect the latex.

When the trees are through running, which is determined by sending out inspectors, the tapper then revisits the trees which he tapped, taking with him two large enameled buckets. Into the one he pours the latex from the cups; in the other bucket he has a small amount of water in which he washes the cup and inverts it beside the tree so that it will be clean and ready for the next day's use.

When this is done he takes his latex to the central collecting station or in some cases directly to the coagulating house. This in brief constitutes the routine life of a rubber gatherer.

The different methods of tapping on the plantation have been studied to some extent. There are two general terms in use for this. " Incision " is done by puncturing the bark, while " excision " means the removing of some of the bark.

Several " incision " methods have been used and are still in use. There was at first a practice copied after the natives' method, of making a large gash in the tree. Later two gashes were joined together in the shape of a V.

Then the practice of pricking the bark was tried. A good flow of latex was secured and the recovery was rapid, but it took too much time to perform the tapping and the latex was difficult to collect. The former difficulty was removed when Bowman recommended his rotating spur-shaped pricker. A single stroke with one of these tools would make a row of incisions running across the bark of the tree. The latex was hard to collect so they combined this method with the one of making a shallow channel in the bark to carry the latex. This however seems to injure the trees.

FIG. 26—MARKING TREES FOR TAPPING

In Ceylon they tried tapping by use of the herring-bone system where each rib was not a channel but four ribs made by a pricker. With the aid of a tapper, the latex can be made first to follow into the central channel and thus be collected.

Bamber suggested a method of incision which produces large quantities of latex. He made two vertical channels on opposite sides of the tree; then, beginning at the top, he made transverse cuts from one to the other extending to the bottom. He would skip a day then make his vertical sections an inch to the right of the original ones and tap the tree in the same manner. This was repeated until the whole circumference of the tree had been tapped. This method has the objection first of consuming a large amount of time; second, that the trees when fully tapped must be allowed a rest period; and third, that a large amount of rubber coagulates on the tree and must be collected as scrap.

At present nearly all the tapping is done by " excision " methods, or the removing of the bark.

The exact time depends somewhat upon the length of time given for the removal of the bark. Four years seems to be the average time allowed for this, although there is a common belief that a longer time should be allowed. But when four years is decided upon, the circumference of the tree is divided into four equal parts, and each quarter tapped by the half-herring-bone method. Each quarter then represents a year's tapping. To preserve the symmetry of the tree the quarter opposite the one first tapped is tapped the second year and the other two sections in successive years.

To mark the tree for tapping, a horizontal line is marked around the tree about four feet from the ground. From this line just five inches apart, if the tree has a girth of twenty inches at this point, two vertical lines are marked down the tree. Then five inches down on one line, a point is marked and, when a line is drawn from this point to the intersection of the other vertical line with the horizontal one, it makes an angle of 45 deg. with the vertical ones. This establishes the angle for cutting and removing the bark.

Fig. 27—Half-Herringbone Tapping

The one vertical line is now made a broad deep channel for conducting the latex, and the other is made deep enough to preserve the limits of the year's tapping. Along the oblique line, a groove is cut deep enough to allow the latex to flow and not to injure the cambium.

That operation constitutes the first tapping. On alternate days generally another thin slice of bark is removed from the lower edge and thus the process goes on until the season of tapping is over and by that time the bark has been removed from this quarter of the tree. Great skill is acquired by some of the workers in this form of tapping. From the following table some idea of the amount of rubber produced per acre can be gained:

Age of trees.	CEYLON. *Per acre.*	CEYLON. *Per tree.*	MALAYAN. *Per acre.*	MALAYAN. *Per tree.*
Years.	*Lbs.*	*Lbs.*	*Lbs.*	*Lbs.*
4-5	50	.4	100	.8
5-6	100	.6	150	1.0
6-7	150	.8	200	1.3
7-8	200	1.2	250	1.6
8-9	250	1.5	350	2.2
9-10	300	1.9	400	2.5

(This table is taken from the report of R. H. Lock.)

Coagulating the Latex

We shall next discuss the handling of the latex which generally contains about thirty-five per cent caoutchouc. This latex is brought into the place of coagulation either in large enameled buckets on the heads of the gatherers or it may be brought by them simply to a collecting station in this manner and from there sent by a railroad system to the factory for treatment.

The first process is that of coagulation.

The substance used to the greatest extent for this purpose is acetic acid. It is said that 99¾ per cent of the plantation rubber is coagulated by this reagent. The amount to be used varies considerably but fortunately it may be used through quite a range and not impair the rubber.

Some one has suggested that an indicator like litmus be added to the latex, which is alkaline, then add the acid until it shows an acid reaction. This has not been found to work satisfactorily in the hands of inexperienced labor. Then too the latex varies and in some instances that amount of acid is not sufficient to cause coagulation as rapidly as desirous.

The safest rule is to make preliminary tests on each batch of latex and thus ascertain just how much acid is required to produce the best results. No rule of thumb is found to work in all cases. Perkin recommended the use of one part of acetic acid to eleven hundred parts of latex.

The acid is first measured out and then diluted with water when it is added to the strained latex and thoroughly stirred, then allowed to stand for a length of time depending upon what form the finished rubber is to be in.

If crêpe is being made the spongy rubber is removed after it has stood about half an hour and is transferred to a washing machine.

If sheet is to be made it is coagulated in shallow pans. These are allowed to stand until the rubber is firm and can be removed in one sheet. This generally takes several hours. These sheets are then passed between smooth rolls running at the same rate with a stream of water playing over them. This is to remove the traces of acid which remain after the coagulation.

When preparing crêpe the washing is done upon a machine which has corrugated rolls and these run at different speeds. The rubber comes out in a long lace-like strip which will dry quickly and is then ready for packing.

The drying is done by one of two methods. The rubber may be hung in an airy room, from which the light must be excluded, and allowed to remain there until it is dry. In moist climates this takes a long period of time. To shorten the time hot air has been blown into these rooms, and thus the drying hastened. Prolonged exposure of the rubber, however, to a high temperature often renders it tacky.

As a still quicker method vacuum driers have been used. Some manufacturers contend that the life or nerve of the rubber is killed by drying in a vacuum. This, however, is a debatable question.

The crêpe after being vacuum dried is then run through a machine which you might say recrêpes it, for the vacuum drier tends to make it fluffy. In some places in connection with the slow drying process they have imitated the smoked rubber from South America by blowing the smoke from burning green wood or cocoanut husks into the drying rooms where either the crêpe or sheets may be hanging. Rubber treated in this manner is known as smoked crêpe or sheet and has been at a premium in the market.

Machines and methods for smoking the latex directly have been patented from time to time but as yet none of these are used to any extent.

Block rubber is made by pressing together either smoked or unsmoked sheet or crêpe. In this form it is handled conveniently but when it comes to the factory for use it must be cut up, which takes labor, and then too it may contain objectionable substances in its interior.

The highest grade of rubber is prepared from strained latex and is known as first latex rubber.

On the large plantations the scrap, that which is coagulated upon the trees and collecting receptacles, is worked up first on mascerating machines, then washed and comes out in a form of crêpe which is graded according to its color.

Tree Diseases and Other Pests

It is well perhaps that we should call attention to some of the pests with which the rubber planter must contend.

The one that causes most trouble is one over which man has not much control, namely the wind. *Hevea* trees cannot be grown in wind-swept districts unless the planter is able to establish a barrier or wind break.

The animals which are a great nuisance are elephants, deer, cattle, pigs, monkeys, and porcupines. If you will observe this list carefully you will undoubtedly come to the conclusion that it would be a difficult task to fence against such a menagerie as this.

Not much damage is done to the *Hevea* by boring insects as the presence of the latex protects the trees from their attack. If a fungus growth should kill the bark in certain areas then some stinging insects will attack the tree at these places.

A species of white ants, however,

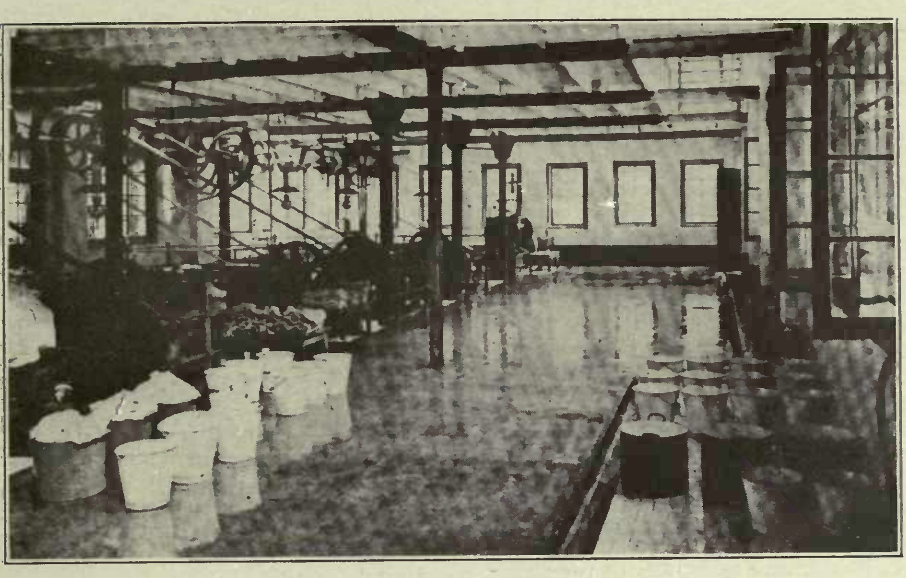


FIG. 28—FACTORY ON RUBBER PLANTATION

must be carefully watched for. They attack the roots of the tree and then eat out the interior. Their presence remains very often unsuspected until the leaves of an apparently healthy tree all at once wither. They can be discovered by digging a small trench around the tree and noticing whether there are any passage ways leading out to their nest which is always located a little distance from their food supply. The fumes of sulphur and white arsenic will kill them.

There is a slug which seems to flourish upon the latex of these trees and often does considerable damage. Painting a band of tar about the tree is sufficient to guard against this pest.

The greatest pests to the planter are those of a fungus growth. Some attack the roots, some the stem and branches and even the fruit.

The fungi which attack the roots are the hardest to deal with. Generally their presence is not discovered until a few trees are blown down due to the killing of the roots. All affected trees must be destroyed and lime forked into the soil. This treatment will kill the pest.

The diseases of the stem are called canker. They are fungi which develop under the bark and tend to destroy it in such a way that it softens and rots. As soon as it is discovered it should all be cut away and then the tree if allowed to rest will heal over the infected area. This same fungus will spread over the tree and attack the seed pods causing them to rot also.

" Pink disease " and " die-black " are terms familiar on the plantation. The affected trees must be diligently sought out and cared for when detected.

Great care must be taken to prevent the spread of any of these pests, and if that is done promptly the task of controlling them is not difficult.

Other Varieties of Rubber Trees

Some other species of rubber trees have been tried in these countries. For instance, *Castilloa* had been under trial in Ceylon, the West Indies, and New Guinea, besides in the localities mentioned in our last chapter.

The *Mannihot* has been tried and is still being worked to some extent. As early as 1883 there were nearly a thousand acres of it under cultivation in Ceylon. The tapping is rather difficult and it has not, therefore, met with any degree of favor from the planter.

Funtumia has been tried on plantations in Africa as we have pointed out in a previous chapter.

Ficus elastica, a rubber tree native of Asia, has been planted in Java and Dutch East Indies but the yield of rubber is so small that in some instances they have been cut down and *Hevea* planted in their stead.

There has been a lack of uniformity in plantation rubber in the past, and strange as it may seem it is the fault of the rubber manufacturers. The planters are anxious to produce the grade of rubber most in favor with the ultimate consumer, whose specifications have been so often changed that the plantation managers have been at a loss to know just what grade is going to suit the trade when they buy their next consignment.

This condition brings to our attention more forcefully the fact that the whole industry is still in the experimental stage.

There are those today who are of the opinion that the plantations in the East are not going to be able to compete with the West in the future. Also that when the large acreage of planted rubber trees are matured and come into full production there will be so much crude rubber on the market that it will not pay a return sufficient to justify the continuance of the industry. However that may be we know that condition is not bothering us at present.

The labor condition is becoming a very serious question on these plantations. A great many of the laborers are imported from India and Java, to such an extent that these two governments are taking steps to stop the emigration of their people.

The native of the Malay States is not of much value in the industry. He is too proud and lazy to work under the direction of a superior. If some task is given him where he feels independent he will work fairly well.

The Chinese have been brought to the plantation and they are somewhat of the same temperament with the exception that they are more industrious and soon come to value too highly their services.

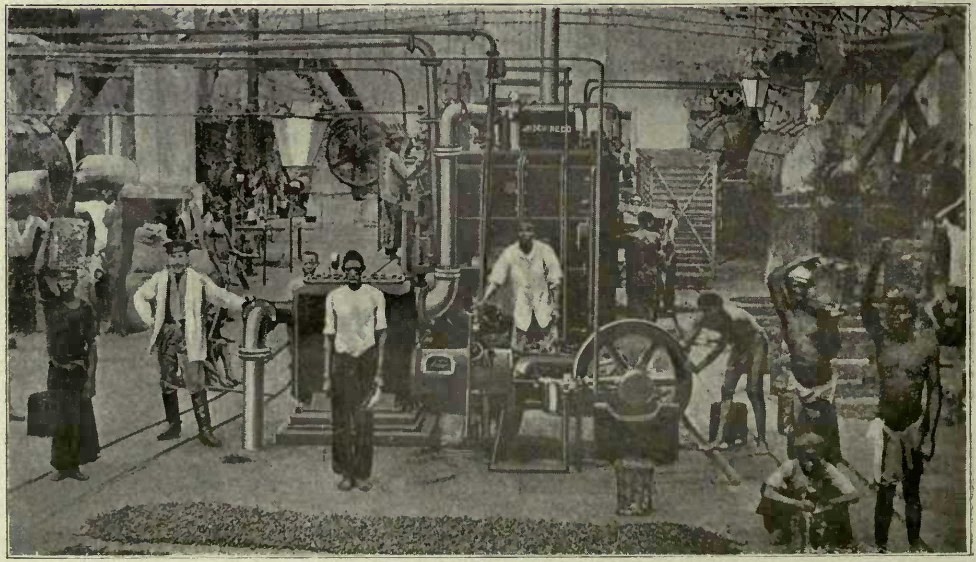


Fig. 29—Vacuum Drying on a Plantation

CHAPTER VI

Discussion of Colloids

Rubber belongs to one of those complex systems of matter known as colloids, which, because of their complexity, have been left comparatively untouched while the more promising fields were being worked. Recent years have seen a change in this attitude, so that we are now in possession of theories which, although investigators differ in their interpretation, are very hopeful.

We are no longer held back by Graham's view that " they (crystalloids and colloids) appear like different worlds of matter and give occasion to a corresponding division of the science of chemistry." Physical chemists are now unanimously agreed that crystalloids and colloids are not different kinds of matter, but are rather different states of matter—that the same may be obtained in the one state or the other depending upon the necessary physical conditions of homogeneity as opposed to heterogeneity. We may therefore define colloid chemistry as that branch of the science having to do with heterogeneous systems of small particles. globulets, films, etc. A brief outline of colloids is in order.

For the colloid state at least two phases must be present. That phase which is divided and distributed (the internal phase) is known as the Dispersed Phase; the external or continuous phase as the Dispersing Medium. We may therefore postulate eight simple types of colloidal solutions, namely:

Dispersing Medium.	*Dispersed Phase.*	*Example.*
Gas	Gas	Impossible, since all gases are miscible in all proportions.
Gas	Liquid	Clouds, mist.
Gas	Solid	Smoke, dust.
Liquid	Gas	Foam.
Liquid	Liquid	Emulsions.
Liquid	Solid	Suspensions.
Solid	Gas	Pumice.
Solid	Liquid	Some gels.
Solid	Solid	Alloys.

Brownian Movements

Let us take a simple case of suspension. If we throw a stone into the water it sinks rapidly; broken up it sinks less rapidly. This has led to a statement that the rate of sinking is dependent upon the size of the particles, which is only true to a certain point. If we go far enough in our subdivision we come to the point where the Brownian movements in the suspension are stable indefinitely, if other conditions which will be explained later are satisfactory. The Brownian movements, so called because of their discovery by R. Brown in 1826 (*Phila. Mag.* 4, 101, 1826), are just noticeable in particles about 0.01 mm. in diameter. Their nature may be readily observed by stirring a very little of an insoluble fine organic powder, for example, carmine, with water and examining under a microscope. The larger particles will be seen to have a fairly regular oscillatory motion, while the finer particles take a more zig-zag course. Zsigmondy (*Zur Erkentniss der Kolloide,* page 107) gives the following figures for the amplitudes of these oscillations for gold hydrosols:

Diameter.	*Amplitude.*
μμ	μ
6	10
10	3-4
35	1-7

(Of course, the amplitude and velocity vary inversely with the viscosity of the dispersing medium.)

These Brownian movements are usually explained by the kinetic theory first advanced by Ramsey (*Chem. News* 65, 30, 1892), or some modification, as being due to the bombardment of the particles in suspension by kinetic vibration of the molecules of the medium. This explanation implies that all the energy possessed by the particles is derived from the medium; on the other hand, there is good reason to believe that it may, at least in part, be due to intrinsic energy of the particles themselves.

Characteristics of Sols

Colloidal solutions are distinguished from what we ordinarily recognize as true solutions by the following characteristics:

1—Osmotic pressure negligible.

2—Diffusion negligible.

3—Conductivity of medium unchanged.

4—Elevation of the boiling point not measurable.

5—Depression of the freezing point not measurable.

6—Peptized or pectized by various salts, ions, electrical charges, etc. (Graham suggested the use of the word peptonize, which because of its use in biology has been changed to peptize to indicate the change from gel to sol and pectize to indicate the reverse change.)

7—Optical characteristics showing distinct heterogeneity.

The question of whether or not colloidal solutions differ from true or molecularly dispersed solutions only in the size of the molecule has been much debated. The writer feels that the difference of opinion simmers down to the interpretation of personal mental picture rather than any real difference in constitution. On the one hand, there are some who conceive a particle as made up of a group of molecules held together by unknown physical forces, probably the same as, or analogous to, electrical forces; on the other hand, others conceive the particle as a molecule held together by much the same forces as are the various atoms which in turn are much the same as, or analogous to, electrical forces. The latter explains the low osmotic pressure and non-diffusion by the size of the particles, the low conductivity, and the little influence on boiling or freezing points to the relatively small number of molecules in a given volume of the solution.

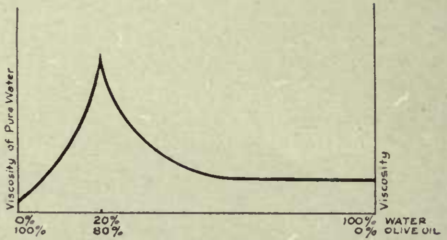


Fig. 30—Olive-Oil—Water Emulsion Viscosity Curve

The former points to examples such as soap; in water, the various characteristics of true solutions may be slightly observable due to alkali present either free or as the result of hydrolysis, but they are negligible; on the other hand, alcohol solutions of soap behave perfectly normally in every respect.

Still another case is that of olive oil-water emulsions. Starting with either as external phase, there is a fairly gradual increase in viscosity until we get to about 80 per cent olive oil and 20 per cent water, at which point the viscosity increases abruptly until it reaches a very high point. This may be explained by a chemical combination of olive oil with water at this point. Looking at it from the purely physical side, why should not the two combine when the other is in excess and give a smooth curve? Explaining, can we not conceive of putting globulets of oil in water or water in oil until the point is reached where the external phase is not sufficient in volume to reach around the internal phase and a rupture must take place, the medium constituting external force to become the internal phase or vice versa? The force required to neutralize the surface tension of the external phase and produce the rupture would be amply sufficient to account for the abnormality in viscosity.

Surface Tension

The condition of heterogeneity implies surface at the interface. The writer has found the following mental picture very helpful in the interpretation of the phenomena.

We learned in our study of physics

that every body of matter attracted every other body; this applies to the smallest particle, even to the atom. The extent of this attraction is represented by the formula,

$$F = \frac{k\,m_1\,m_2}{r^2}$$

where

F is the attractive force,

m_1 and m_2 the mass of the respective bodies,

r the distance separating the bodies,

k is the constant.

Because the mass of the earth is so great and we are so accustomed to interpret it in terms of bodies separated by microscopic rather than submicroscopic distances we are apt not to appreciate its true significance unless it is called to our attention. Upon inspection, however, it is realized that as r becomes extremely small, even though the mass of respective bodies is very small, the extent of this force may become very great indeed, even approaching infinity as r approaches zero, which it probably does not do even on the interior of the atoms themselves. This force may well be the force which holds bodies together; indeed, it may well be the source of chemical valence.

The distance through which this force may operate is very indefinite, but the sphere limiting its radius of action is at least larger than the particle itself. Other particles within the sphere of attraction affect it and are affected by it; those outside do not. Let us then single out a molecule in the interior of a liquid. It exerts a sphere of attraction equal in all directions. (In speaking of this sphere of attraction, we do not necessarily wish to imply a perfect sphere. If the molecule happens to be a chain structure, the sphere would follow the general contour of the chain.) Within this sphere there will be other molecules, approximately an equal number in all directions, which in turn build up another sphere, and so on until we go beyond the surface. A molecule at the center therefore has the same counterbalancing attractions from all directions and the net force tending to displace it is consequently zero, causing equilibrium in the molecule.

These series of concentric spheres are thus continued until we reach the surface. The molecule on the surface has many molecules within the sphere of attraction on the interior, but relatively few on the exterior. It is consequently attracted to the interior very strongly without counterbalancing attraction from the exterior. The result is a high inward pressure. Just as a high outward pressure must be restrained by a high tension on the container walls, this inward pressure must result in a high surface compression in the surface film, which tends to cause the liquid to decrease in volume. This surface compression is incorrectly known as surface tension, and may be observed when we " heap " a spoon with liquid, or float a needle on the surface of water, provided it is laid down carefully.

Any increase in surface is attended by an increase of free energy at the surface; conversely, decrease in surface results in a decrease of free energy. Disintegration, evaporation, etc., require energy; agglomeration, condensation, etc., give up energy and are spontaneous. Large drops and crystals grow at the expense of smaller ones.

We have no adequate means of measuring surface tension. It may, however, be considered in connection with osmotic pressure, which, if it acts in any manner similar to gas pressure, must require a restraining force. What other force than this surface tension can there be? And since the osmotic pressure is outward, there should be a lessening of the pressure inward causing the volume of the solution to be greater than the volume of solvent, which always happens. In the case of some solutions, the osmotic pressure is considerable; the surface tension must therefore be even greater.

Willard Gibbs pointed out the obvious result of these forces; namely, that there is no definite boundary at which the one phase leaves off and the other begins. True, the zone between that which is distinctly composed of the one phase and that which is distinctly composed of the other phase may be very slight; nevertheless there is that zone at every interface where the two phases intermingle, and where surface forces come into play. The greater the surface tension the thinner the zone, i. e., the less chance to intermingle; whence it will be seen that anything which tends to decrease the difference in surface tension between two immiscible phases will cause them to mix more readily; the converse is likewise true. This is of great importance in the selection and use of protective colloids. Surface energy equals specific surface times surface tension.

From the picture drawn, it is evident that the center of the liquid is under greatest pressure. In the case of true or molecularly dispersed solutions, the concentration should be greater at the center, as is found to be the case with, for example, most inorganic salts. On the other hand, where the solution is only apparent (i. e., heterogeneity), as, for example, soap in water, there will be a greater concentration of the solution at the surface. Increase in surface concentration will result in decrease in surface tension and vice versa. Where we have this difference in concentration between the surface and the interior, we have what is known as adsorbtion. If the surface concentration is in excess, as is usually the case, we have positive adsorbtion. If such a solution is shaken with a very fine powder giving a very large surface (size of particles is not necessarily a criterion, since, as in the case of various blacks, the material may be spongy and thus present an enormous amount of surface in the capillary pores) nearly all of the solution may be removed from the solvent. Surface deficit must necessarily be very slight, since the limit must necessarily be pure solvent in the surface, which would give rise to negative adsorbtion; indeed, even this case may be regarded as positive adsorbtion of the solvent.

Adsorbtion comes to an equilibrium. Thus, if a given volume of solution of certain concentration is shaken with a weighed amount of adsorbant until equilibrium is reached and is then diluted, the final concentration of the solution will be the same as if the dilution had been made before starting. This gives rise to the adsorbtion equation,

$$\frac{x}{m} = k \, c \, \frac{1}{n}$$

where
x is the weight of substance adsorbed,
m the weight of adsorbant,
c the volume of the concentration after equilibrium,
k and $\frac{1}{n}$ are constants.

The question as to whether adsorbtion is chemical or purely physical combination has been much debated. Indeed, the discussion simmers down to a matter of viewpoint. It seems highly probable that both forces are akin to electrical attraction and therefore may easily be the same.

Cataphoresis and Electro-endosmos

In no place does the phenomenon produced by electrical charge play a more important role. At the interface between two phases there is always a potential difference. If a liquid, say water, is placed in two vessels connected by a capillary tube and subjected to electrolysis it will flow with the current; if finely divided particles of an insoluble powder such as metal, sand, etc., be suspended in the liquid, it will move instead. This phenomenon is known as cataphoresis. If the flow is through a semi-permeable membrane, it is known as electro-endosmos. There are three cases possible.

1—The particles are poor conductors and have slight tendency to coalesce. Such particles will move sluggishly toward the electrode and will congregate around it. Those actually coming in contact with the electrode will deposit a part of their charge, but not all of it; the others, being such poor conductors as not to be able to transfer their charge, will retain it, and when the current stops will mutually repel each other as far as possible, thus diffusing themselves throughout the liquid substantially as before being subjected to the influence.

2—Particles which are good conductors but have little tendency to coalesce will move up to the electrode, get rid of their charge and take on one of opposite sign, after which they will start for the other electrode.

3—Particles which are good conductors with a tendency to coalesce will move up to the electrode, discharge, and be precipitated.

We have discussed the individual conditions which bear upon colloidal phenomena. We see that colloids are systems consisting of at least two distinct heterogeneous phases, one of which is extremely finely divided and dispersed in the other and which is more or less affected by Brownian movements, depending upon the viscosity of the dispersing medium. This fine state of division gives rise to an enormous extent of surface interface, which, because of its nature, gives a correspondingly large amount of free energy in form of surface energy and electrical energy. The activity of this energy probably contributes the Brownian movements and, in being neutralized, gives rise to adsorbtion. We can postulate the behavior of solutions, that is, the conditions of peptization and pectization.

Since the formation of a large amount of surface involves an enormous amount of free energy which is neutralized in part by adsorbtion, we have a basis for Freundlich's assertion (*Kapilarchemie* 52, 154, 1909) that adsorbtion tends to lower the surface tension of the adsorbing phase, from which it follows that any substance which is adsorbed by another tends to disintegrate and peptize the latter. In making this statement, however, we must bear in mind that, since adsorbtion depends on the surface and disintegration depends upon the cohesion between the particles, there may be no apparent connection between the two. Thus the same mass of porous material is much more easily disintegrated than if it occurs in a more dense form.

Bancroft (*Jour. Phys. Chem.* 20. 85, 1916) has discussed this subject in detail. He says: "We may have peptization by a solvent, by a dissolved non-electrolyte, by an ion, by an undissociated salt, by a colloid."

As we raise the temperature, adsorbtion decreases, but the cohesion between the particles also decreases; thus glass, coagulated albumin, etc., are peptized by water, provided the temperature is raised to a point where the cohesion between the particles is sufficiently small to be exceeded by the tendency to absorb the solvent.

One of the many examples cited in the case of a dissolved non-electrolyte is the action of sugar in preventing the precipitation of ferric hydrate when ferric chloride is treated with ammonia.

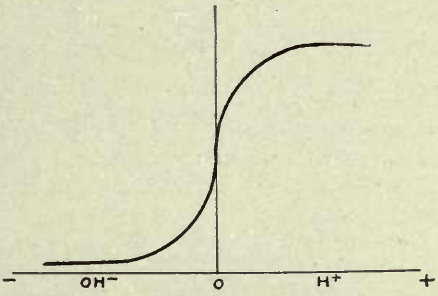


Fig. 31—Ion Curve

The action of ions is closely associated with their supposed electrical nature. If we add a small amount of an electrolyte to a solution, precipitation takes place. Ions carrying a charge opposite in sign to the dispersed phase are adsorbed more rapidly, thereby neutralizing the charge which keeps them apart. Very soon the place is reached where the charge which keeps the particles apart is neutralized, and instability results. Beyond this point, the adsorbtion of the first ion varies but slightly with increase in concentration, but the adsorbtion of the ion of opposite charge increases until we get a corresponding excess of the opposite charge and consequent peptization by the salt. In general, the action of ions follows Schultz's law that the higher the valence the greater the influence of a single ion. This rule is disturbed, however, by the preferential adsorbtion of certain ions.

The examples of peptization by a colloid are without number in our every-day experiences. We have to go no further than the use of soap for washing; the insoluble dirt adsorbs the soap film and is peptized by it, after which it can be easily washed away.

It is not the purpose of this work to go into the study of colloids. In giving this discussion, the writer has merely attempted an explanation of some of the fundamental principles underlying the behavior of colloids so that their influence on the rubber colloid may be appreciated. Students are earnestly requested to study some of the text books and numerous articles on colloids, as well as the application of the principles to other industries, such as the cellulose, glue, and tanning industries.

CHAPTER VII

Colloidal Action of Crude Rubber and Its Application in Rubber Manufacture

The latex as it comes from the tree is a milky white fluid which in the light of colloidal chemistry should be classed as an emulsoid in contrast to a suspensoid; namely, a heterogeneous system consisting of two distinct liquid phases. The dispersing medium is water and the dispersed phase consists of globules of caoutchouc ranging in size from 1μ to 2μ. This emulsion is made fairly stable by the presence of certain resins, albuminoids, proteids, sugars, mineral salts, etc., which act as protective colloids.

This latex upon examination shows pronounced Brownian movements. As is the case in nearly all hydrosols, the dispersed phase bears a negative charge as is shown when the hydrosol is subjected to electrolysis, when the globules migrate to the anode region. From this behavior, we may postulate that upon the addition of a kation, these globules will tend to be precipitated while the addition of anions will tend to make the emulsion more stable.

It is quite possible that the caoutchouc itself in the latex is positively changed, but that it has adsorbed enough of the protective colloids which are negatively charged to more than balance the positive effect and thus give to the globule the effect of being negatively charged.

Therefore anything which tends to destroy this protective colloid, tends to destroy the negative charge which gives stability to the emulsion.

Let us now turn our attention to a discussion of the manner in which these principles are applied in the crude rubber industry.

Preservation of Latex

First let us consider the preservation of the latex where it is not desired to coagulate it immediately. We find the general practice is to add ammonia. This was first done without the knowledge of any scientific reason as a basis for it; now, however, it may be explained by the principle which we have just mentioned. The ammonia introduces hydroxyl ions, bearing negative charges and these tend to increase the potential difference between the two phases and thus increase the stability of the emulsion.

Next, we shall endeavor to show how these principles are applied in the coagulation of latex. To do this we shall divide the different means of coagulation into the divisions: 1—Mechanical; 2—Electrolytic; 3—Dilution; 4—Natural; 5—Heat without evaporation; 6—Heat with evaporation; 7—Chemicals.

In the mechanical coagulation of rubber, we simply take advantage of the fact that in the latex there are two distinct phases of different density. Therefore by centrifuging the latex, we are able to effect a separation. Rubber obtained by this method compares favorably with the rubber obtained by other means, but the process is a tedious one and rather expensive also.

The electrolytic method is one of theoretical interest only. As the latex is such a poor conductor of electricity, and the globules simply collect in the region of the anode, unless the voltage is very high those in actual contact with the anode will be the only ones which will discharge and thus precipitate.

Coagulation by dilution in a great many cases produces unfortunate results, while again it is used to advantage. The necessity of collecting latex out in the open in a region where the precipitation is so abundant makes dilution of the latex by rain water inevitable at times. Such latex coagulates in much the same fashion as cream separates from milk which has been diluted. Then in the case of cup washings, the latex which has been washed out from the cups is saved. On a few small plantations where the quality is not a consideration, and in places where better methods are unknown, this method is used as a regular procedure. The reason for the precipitation undoubtedly lies in the fact that the protective colloids are more or less soluble in the increased volume of the dispersing medium. When these protective colloids are removed, it results in the precipitation of rubber. While comparatively little is known as to why certain of these materials which make up protective colloids are essential, it is a fact that their absence results in an inferior product. Consequently this method is by no means satisfactory and is not employed where its use may be avoided.

When the latex is allowed to stand for some time, it will coagulate spontaneously. This is no doubt due to the formation of acid in the latex from causes which will be discussed in a later chapter. The acids which are produced furnish the necessary hydrogen ions to cause the coagulation of the rubber. Due to the fact that the conditions cannot be or are not regulated correctly, an inferior product invariably results.

If the latex is subjected to heat without evaporation, we have a combination of results similar to dilution, that is increased solubility of protective colloids, and the formation of acids as in natural coagulation, which is probably still further complicated by hydrolysis. This method of coagulation is of little practical importance.

When the latex is evaporated by addition of heat, coagulation results. There we have much the same conditions as in the case of heating without evaporation, that is in the formation of acids and hydrolysis but we have in this method the advantage of uniform conditions such as temperature, time, and also the fact that the protective colloids which are soluble cannot be removed from the rubber. Usually, too, in the case of South American rubbers, the process is carried on in the presence of smoke which contains various acids and alcohols. These tend to facilitate the coagulation and at the same time inhibit the development of bacteria.

The foregoing methods are all primitive and whatever merits they may possess are accidental.

Coagulation by Chemicals

By all means the most important is the coagulation effected by chemicals. The ones in most common use may be classified under the following heads: Acids, salts, alcohols and ketones.

We would naturally expect all acids to have a coagulating effect in proportion to their degree of ionic dissociation since they owe their power of coagulation to the concentration of hydrogen ions. The question of selective adsorbtion plays no role in this because the hydrogen ions are the same regardless of their source. Strong acids should therefore be better coagulants than weak acids since they possess a higher degree of dissociation. Therefore we should expect to find the highest dissociated acids being used for the above purpose. These are muriatic, nitric, and sulphuric acids. In actual practice, however, the first two are not permissible.

Muriatic acid, while it has the desired coagulating effect, also has a deleterious effect upon the rubber. This might be explained upon the ground that as a halogen acid, it acts upon the polyperene molecule at the double bonds thus tending to form addition products.

Nitric acid also possesses a marked degree of coagulation but here the strong oxidizing power of the acid renders it useless. Sulphuric acid, however, is used quite extensively as it possesses neither of the objections which characterize the other two.

The question naturally arises, why should acetic acid be used in preference to sulphuric? It must be borne in mind that acetic, however, is by far the strongest or most highly dissociated of the so called weak acids. It furnishes, therefore, the necessary concentration of hydrogen ions very nearly as readily as the sulphuric acid. All of either acid must be completely removed from the coagulum. Sulphuric acid must be entirely removed by washing, and to remove it completely requires prolonged washing, which experience has shown impairs the rubber. With acetic acid, on the other hand, it matters not whether all the acid is removed by washing since any that remains will be volatilized and thereby removed in the process of drying.

The other organic acids have the two objections, first, that they are too feebly ionized and secondly, that their cost makes them prohibitive.

Under salts, those most commonly used are sodium chloride, alum and soap.

If we apply the law of Schulze, that is, that the higher the valency of the kations in a hydrosol, the greater will be its precipitating power, then we should use those salts which not only furnish a high concentration of kation but also those which possess a large valence. Of course, this condition may be disturbed by selective adsorbtion.

We find sodium chloride is used only where the more primitive methods are in vogue. It is an extremely common substance and consequently was available for primitive experiments. It accidentally possessed the property of being highly dissociated, having the necessary number of kations to make it effective as a coagulant. On the other hand, where more scientific methods of reasoning have been brought to bear, we find alum is used more or less extensively. Then we get a much higher electrical charge with a small number of ions. Soap has found little application as would naturally follow from what has been stated above, namely: it possesses a very low degree of ionization and a low charge on the kation.

The use of salts is in no case desirable because if any remain in the rubber they will undoubtedly undergo hydrolysis and the resulting products are likely to be detrimental to the rubber. Their complete removal is almost impossible even with excessive washing.

In the use of alcohols and ketones coagulation is effected, no doubt, because these substances have the power to dissolve the protective colloids and thus allow the rubber globules to coalesce. It is said that a much better grade of rubber results when either ethyl alcohol or acetone is employed; this being no doubt due to the fact that undesirable substances are dissolved out while the more desirable ones remain in the rubber.

In the case of Guayule, we are confronted by a special proposition. This, coming as it does from the shrubs, cannot be obtained by the ordinary means of tapping. The process is largely a mechanical one, but the principles of peptization and pectization are both taken advantage of in this process. The shrubs are macerated in pebble mills and then digested with an alkaline solution. This pectizes the rubber and makes it possible to remove it. After this it is precipitated. The process is largely secret.

Application of Colloidal Chemistry

Next in order we shall discuss a few of the applications of colloidal chemistry to rubber manufacture.

Considering mixing, we must first call attention to the fact that in breaking down the rubber on the mixing mills, we increase the surface. Inasmuch as the colloidal action of the rubber does play a part in its behavior, the extent to which we increase the surface by this breaking down process will have a proportionate effect upon this action.

Among our compounding ingredients we have some materials which have high adsorbtive power, others which are comparatively inert, and still others which are more or less adsorbed. Consequently we may expect a difference in the behavior of the stock depending upon the order in which the compounding ingredients are added. For example, let us take a compound containing rubber and sulphur, a highly adsorbtive material, and a material capable of being easily adsorbed. If the easily adsorbed material is one that directly affects the rubber itself, the probabilities are that it should be added first in order that the full extent of the adsorbtive forces between it and the rubber may be realized. If, on the contrary, the highly adsorbtive material has been added first, it would have no doubt adsorbed the rubber and thus satisfied or at least materially lessened the adsorbtive force which the rubber possessed.

It may be noted in passing that there are a few materials which have a great influence upon the physical properties of the cured compounds where they are used; and these substances have a high adsorbtive power. As the most notable examples of this phenomenon we may mention zinc oxide and lamp black. The latter is one of the best adsorbents known and has the property of increasing tensile strength of rubber compounds more than any other substance. Without exception the materials used in rubber compounding which have slight adsorbtive power are practically inert and serve merely as fillers.

Of course we must not fail to remember that these materials which we have mentioned which have a great absorbtine power, likewise possess an enormous surface due to their fine state of division and their porosity. On the other hand, the others are comparatively coarse and more compact.

The theory has been advanced and has received considerable support that the swelling of rubber in benzene may be accounted for as follows: The rubber possesses a more or less cellular structure. Therefore, when it is placed in benzene, the solvent enters these cells and adsorbs certain substances therein and thus produces osmotic pressure, which distends the individual cells until they burst open and then disperse through the solution. If this theory is correct, it naturally follows that when the solvent is evaporated, the residue should possess different properties than the original rubber. We know that this is not true.

A much more reasonable explanation may be found in our theory of peptonization advanced in the last chapter. From this we would explain the phenomenon of rubber solution as follows:

When rubber is placed in the solvent, the latter is adsorbed by the rubber. The volume of the solvent adsorbed causes the swelling of the rubber until finally sufficient has been adsorbed to break up the cohesion between the rubber particles and disperses it through the entire solution. When such a solution is evaporated, the particles remain unruptured and will finally go back to their original state. This is more in accordance with what actually happens.

Furthermore, if the rubber has been first broken down upon the mill, and thus its surface increased, it will adsorb the solvent more easily and give a solution in a shorter time.

The role of colloidal phenomenon, as it is applied to vulcanization and to reclaiming will be considered in the following chapters.

CHAPTER VIII

Different Means of Coagulation

While discussing the different varieties of rubber which come from the various sources, we have called attention in each case to the methods used in their coagulation. Some of these have been primitive and most have lacked a scientific basis. The result of this has been that some rubbers from certain localities have been very good and uniform while those from other places are characterized by lack of uniformity, and therefore are expensive experiments most of the time.

Of course, at present, the methods of control are more uniform on the plantation and as a result the rubber from these sources is the most uniform found in the market. That leads us to suspect that the wide variance in native rubbers is occasioned principally by the lack of uniform methods of coagulation. This has led men to investigate the different methods in use, with the idea of trying to find some more satisfactory process than is at present known. They have been guided by observations of conditions which exist in places from which the various grades are obtained.

We know the rubber from the Amazon to be the most uniform of any wild rubber on the market. When we observe the methods by means of which the seringueiro collects and coagulates the latex from the Hevea and thus obtains Para rubber, we come to the conclusion that the process wherever and by whomever used is one that will produce a uniform product. On the other hand, when we observe the product from Africa and notice the great differences even in the same grades, we are satisfied in our own minds that the methods used must be at fault.

The whole trade recognizes that we have not at present any method of coagulation that is entirely satisfactory. This is very apparent when we realize that even the method which produces the most uniform rubber of all, namely, the plantation, is at present under severe criticism, and chemists are employed to make a thorough study of this whole question in order to substitute a better one.

This study is based upon certain principles of colloidal chemistry and it is hoped that by the aid of these investigations we are going to be able to bring forth something new and better. We know that the stability of latex from different sources varies, and we have come to the conclusion that this is due to the different size of particles in the different emulsions, to the electrical charge, and to the presence of protective colloids, etc. Fickendey (*Z. Chem. Ind.* Kolloids, 1911, 8, 43) calls attention to the fact that coagulation in general consists in the removing of the proteins or peptones, which serve as protective colloids, and then the neutralization of the electrical charges. Upon the addition of acid to the latex, we effect coagulation in all cases except Funtumia. This latter fact has been explained upon the ground that it is a case of a peptone acting as the protective colloid instead of a protein. However, Spence has shown that the size of the particle in the Funtumia latex has a great deal to do with its stability also, for he removed the peptone by treatment with trypsin and no coagulation resulted. (*Quar. Jour. Reprints,* 1907, 9, 5.)

The Brownian Movements are apparent in the latex and V. Henri (*Le Caoutchouc et la Gutta Percha,* 1908, 5, 2405) took advantage of this to study the effects of acids and alkalis upon it. He found that the addition of acids greatly reduced the velocity of the rubber particles, while alkalis had much less effect. When the acid was increased, the particles seemed to form in a sort of network.

This is interesting from a scientific point of view, but its influence upon the manufacture may be slight, yet today we are also having it studied from the manufacturer's side.

It was to study this problem from this angle that Eaton and Grantham, in the Department of Agriculture of the Federated Malay States, started on what might be called the first scientific investigation of this subject of coagulation and its effect upon the rubber obtained for manufacturing purposes.

The manufacturer had observed the difference, which we find in the mechanical curing of rubber from different sources and in fact from the same source. Some forms of rubber from a certain plantation will cure in a way different from that of another variety from the same place.

Corresponding grades from different plantations likewise show different peculiarities in curing. This of course raised the question as to what caused this variance. It led some men to think that in order to use any rubber intelligently, one must know the complete life history of it: where it came from, how it was gathered, how it was coagulated, how it was treated after coagulation, what form it was put into, how old it was, and many more facts.

In the first experiment of Eaton and Grantham, which appeared in the *Agricultural Bulletin* of the F. M. S., they call attention to two facts.

(1) That in plantation rubbers there is a great variation, but this comes largely in the rate of cure and not in mechanical properties, since similar mechanical properties can be obtained in the vulcanized material, provided the correct rate of cure of the rubber under specific conditions is known.

(2) That this variation in rate of cure or vulcanizing capacity is due to some substance existing in the latex, or formed subsequently, which in the prepared raw rubber acts catalitically as an accelerator, and that the rate of cure of raw rubber depends on the amount of this substance remaining in the raw rubber, which again depends on the mode of coagulation and preparation. In trying to establish these, they selected what they regarded as a set of uniform conditions for determining what is known as the "optimum cure," that is, the cure which shows the maximum product of elongation by tensile strength. They cured all of their samples at a temperature of 140 C. and took test strips every fifteen minutes. The sulphur content was 10 per cent of the whole mixture.

The first tests were made upon Plain Crepe and Smoked Sheet. Both of these showed the optimum cure at three hours. At this point they received a sample of "Byrne cured slab," and when this was tested out it showed the "optimum cure" at one hour and fifteen minutes. Here we have a rubber which cures an hour and forty-five minutes more quickly than plain or smoked sheets, and yet is obtained from the same latex. You may immediately realize what this means to the manufacturer of today.

Here two questions presented themselves: (1) Was it due to the Byrne fumes, or (2) the form in which the rubber was prepared? They then prepared what is known as a Byrne Loaf (this is made by rolling sheets cured by the Byrne fumes around a stick, thus building up a solid cylinder of superimposed sheets); this rubber never completely dries in this form and has to be creped and dried before vulcanizing. The results on this loaf, and also upon pressed sheet, showed the optimum results at two hours and forty-five minutes. This is practically the same time as that required for plain crepe or smoked sheet, and therefore points to the fact that it is not the Byrne fumes which cause the variation in the rate of cure.

A sample was then prepared by

coagulating the latex in thin layers in shallow pans in a smoke house and thus superimposing further layers daily for a period of a week. By this method a slab of rubber resulted, and when this was cured and tested it came to the optimum test in an hour and a half. In other words, a rapid curing rubber had been produced, and we are almost safe in saying from these two tests that the rate of cure is due to the form rather than to the fumes. Further tests revealed the fact that smoked sheets vulcanized more slowly than plain sheets, and hence the conclusion that smoking has a tendency to retard the rate of cure. We may therefore call attention to the following facts:

(1) Slab rubber smoked by Byrne fumes or rubber coagulation by smoke, by superimposing layers of latex, cures much more rapidly than plain crepe or smoked sheet.

(2) Unsmoked sheet cures more rapidly than smoked sheet or plain crepe.

Latex was next placed in a large wooden box with movable partitions, so that all might receive the same treatment during coagulation; then from the coagulum the following samples were prepared:

(*a*) Smoked sheet, which showed its " optimum cure " in two hours and forty-five minutes.

(*b*) Smoked sheet, creped when dry; this required two hours and forty-five minutes.

(*c*) Smoked slab, "optimum cure," one hour and forty-five minutes.

(*d*) Unsmoked sheet, " optimum cure," two hours and forty-five minutes.

(*e*) Unsmoked sheet, creped after drying, " optimum cure," two hours and forty-five minutes.

(*f*) Unsmoked slab, " optimum cure," one hour.

The conclusions to be drawn from these tests are that creping of dry sheet has no effect upon rate of vulcanization; also, that slab is the most rapid curing form of rubber; and lastly, that smoking will retard the rate of cure on slab. To explain this behavior, two theories present themselves:

(1) That the latex contains, in addition to the caoutchouc, some constituents which influence the rate of cure of the rubber, this substance not being precipitated by ordinary coagulation. Consequently, the greater the quantity of serum remaining in the rubber, the greater will be the quantity of this substance present in the raw rubber. If this is the case, the effect of smoking is apparently the destruction of this substance.

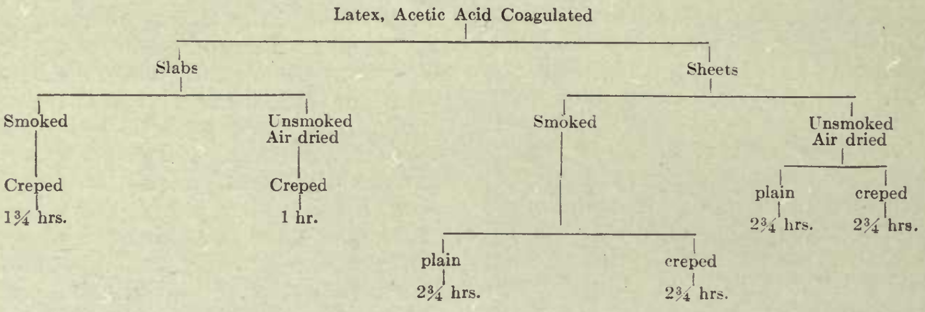
(2) It may be, however, that this substance does not exist in the latex, but is formed from some constituent of the latter. In this case the retention of the serum in the rubber would appear to encourage the formation of the catalytic substance. Our ordinary methods of analysis of crude rubber, of course, will not reveal the presence of these substances. For instance, we determine the nitrogen in the rubber and calculate it all as proteins and this may be far from the actual truth of the way the nitrogen really does exist. We do know that certain amines have an accelerating effect upon vulcanization, and it follows that perhaps some of these proteins do decompose into amines, and therefore the greater the amount of serum left in the rubber, the greater will be this effect. To strengthen this theory, Eaton and Grantham observed that we get slow curing rubbers from latex treated with preservatives, or from smoked rubbers, which act in the same way. If this change is caused by an enzyme, then the same may be expected for the preservative, or smoke would of course kill it and thus produce a slow vulcanizing rubber.

That this material is present in the latex is also substantiated by the fact that synthetic rubber is very difficult to vulcanize.

Another fact pointing in the same direction is that air-dried slab is the most rapid curing and also has the most serum remaining in the rubber.

Fine hard Para is rather slow curing, due to the fact that the smoke in coagulating has its maximum ef-

TABLE 1



Time Required for Curing Various Kinds of Rubber.

fect. The " optimum cure " requires from two and one-half to two and three-quarters hours.

The rate of cure of samples from different states shows quite a variance due to many causes, e. g., dilution of latex, working of rubber, thickness of rubber, smoking, rapidity of drying, amount of coagulant, etc. (*Agricultural Bulletin*, Federated Malay States, March, 1915.)

The lack of uniformity in these rubbers is of great importance to the manufacturer, for if by regulating the preparation of the rubber from the latex we are able to procure a rapid curing rubber, then a great deal of cost in the manufacture is saved and a greater output is also made possible with the same equipment and number of men.

Eaton and Grantham have also conducted experiments to find the extent to which lack of uniformity in the mechanical method of procedure in the preparation of rubber from the latex caused variation in the product. (*Agricultural Bulletin*, Federated Malay States, 111, 218, 1915, et seq.) They found:

(1) That after the rubber has once been reduced to a thin sheet, excessive creping has little or no effect.

These conclusions were based upon the results obtained from passing different lots of the same rubber through the creping machine five, ten, fifteen, twenty, and twenty-five times, respectively. Excessive maceration, however, does seem to have a slightly retarding effect upon the rate of cure. An interesting feature of the experiment was shown by repeating the tests on mixtures out of these samples, made eight months later. These tests indicated somewhat slower cure in the sample creped twenty-five times. This is particularly interesting because of the apparent recovery, which has been so commonly noticed after rubber broken down on the mills has been allowed to stand.

(2) That the use of more acid than necessary to produce coagulation has the effect of slightly retarding the cure. The use of sodium bisulphite has no effect.

(3) That samples of rubber from the same latex were taken at different stages in the preparation as follows: *a,* Coagulated slab and allowed to drain; *b,* after rolling once; *c,* rough crepe; *d,* thick crepe; *e,* thin crepe.

These samples were kept for twenty days; then samples A, B and C were made into thin crepe and all five samples were dried, after which they were compounded similarly and cured. The " optimum cures " reported were: *a,* 1 hr., 30 min.; *b,* 2 hr.; *c,* 2 hr., 30 min.; *d,* 2 hr., 45 min.; *e,* 3 hr., thus substantiating their contention that each step of the process seems to have a retarding influence on the cure.

Continuing on this line, they went further into the effect of drying in hot air driers up to 2 hr., at 150 deg. F., samples being taken practically as before and also a sample being taken from the drier every hour. All of the samples, which had been in the drier required 3 hr., 15 min. for curing or 15 min. more than the time required for thin crepe.

(4) That tests of the product from the estate handled by the same methods were quite uniform. One interesting thing was indicated through the course of these tests. On two occasions the trees were permitted to rest longer than usual because of rain for a whole day; on another the tapping was late. The quality of rubber obtained from these subsequent tappings was above the average.

(5) That the following experiments indicated the effects of leaving the coagulatum in slab form for ten days before curing:

a Block prepared as usual on the day following coagulation, cured in 3 hr., 15 min.

b Block prepared after leaving coagulum from some of the same latex in the slab form ten days before creping, blocking and drying, cured in 1 hr., 15 min.

c Slab, prepared the same as B, cured in 1 hr., 15 min.

Sodium bisulphite had no effect when used in parallel experiments. The mechanical qualities of *a* were also inferior.

By mixing proportionate amounts of fast and slow curing rubbers together, the rate of cure may be adjusted to uniformity. They explain the uniformity of fine hard Para by the fact that a single ball represents latex collected day after day for a period of months. In passing, it is but fitting to note that many compounders prefer to use a mixture of rubbers in their stocks so that the variation in different lots of each may be averaged and a more uniform product obtained.

An attempt has also been made (*Agricultural Bulletin*, Federated Malay States, IV, 1, 1915) under the direction of Mr. Eaton to determine the influence of the nitrogen content on the cure with the possible view of regulating this factor to the best advantages. Their data may be summarized as follows:

Type of Rubber	N_2	Cure
Smoked sheets	0.445 per cent	3 hr.
Smoked sheets after creping	0.441 per cent	3 hr.
Smoked slab after creping	0.451 per cent	1¾ hr.
Unsmoked sheet	0.423 per cent	2¾ hr.
Unsmoked sheet after creping	0.434 per cent	2¾ hr.
Unsmoked slab after creping	0.321 per cent	1¼ hr.
Thick smoked slab	0.425 per cent	1½ hr.
Thin smoked slab	0.398 per cent	1¾ hr.
Thick smoked sheet	0.400 per cent	2½ hr.
Thin smoked sheet	0.416 per cent	3 hr.
Thick unsmoked slab	0.210 per cent	1¼ hr.
Thin unsmoked slab	0.352 per cent	1½ hr.
Thick unsmoked sheet	0.386 per cent	2½ hr.
Thin unsmoked sheet	0.394 per cent	3 hr.
Unsmoked slab dried externally, results calculated on 82.7 per cent dry rubber	0.307 per cent	
Sliced slab heated to 100 deg. C. till dry	0.240 per cent	
Dry crepe from slab (dried without heating)	0.218 per cent	

Results on the following data calculated on the basis of the dry rubber present:

Wet slab 2 hr. after pressing	0.600 per cent
Wet slab after drying thirteen days	0.324 per cent
Dry crepe from slab	0.220 per cent
Wet crepe made immediately from wet slab	0.396 per cent
Above crepe when dry	0.360 per cent

We may summarize the above data in the following conclusions:

(1) Among smoked rubbers from the same latex the nitrogen content is constant, although the rate of vulcanization varies considerably between slab and sheet. Smoking appears to fix the nitrogen.

(2) Among unsmoked rubbers from the same latex there is a considerable variation in the nitrogen content of the rubber after creping preparatory to the vulcanization process. It is small in the case of rapidly vulcanizing rubbers and larger in the case of the more slowly vulcanizing ones.

(3) The low percentage of nitrogen in rubber prepared as unsmoked slab is attributed partly to loss in the gaseous form during the superficial drying of the slab, and partly to the washing out of nitrogenous decomposition products when the slab is creped prior to vulcanization.

(4) Since rapidly vulcanizing smoked slab rubber contains as high percentage of nitrogen as slowly vulcanizing sheets, the actual loss of nitrogen cannot be the cause of rapidity of vulcanization, although it would appear from the results of the unsmoked rubbers that rapidity of

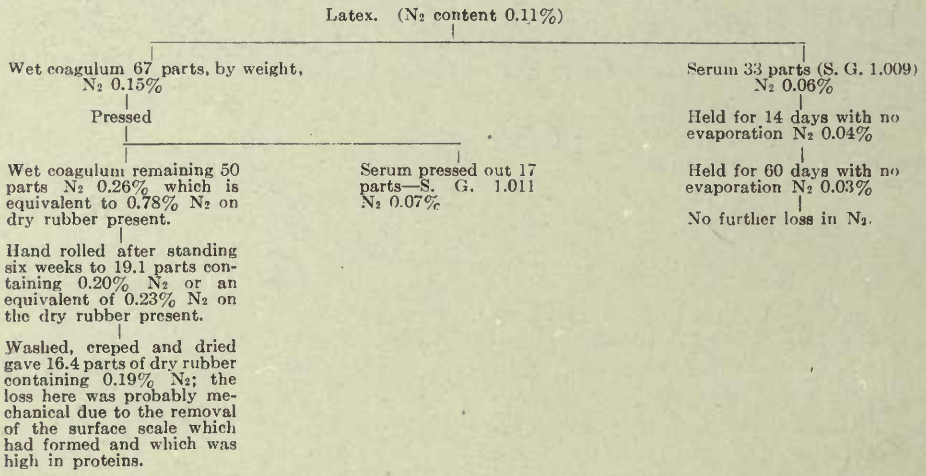
vulcanization and loss of nitrogen are in some way associated.

Eaton and Day (*Agricultural Bulletin,* Federated Malay States IV, 350, 1916) have followed the change of the nitrogen content through the different stages of handling the latex. The results are summarized in the accompanying chart. (Table II.)

The same coagulum, converted directly to sheet and crepe, on the day following coagulation contained 0.40 per cent nitrogen, or about twice as much as the other.

In 1912 Whitby presented before the Congress of Applied Chemistry, a paper in which he made the claim that the natural coagulation of Hevea latex was brought about by a coagulating enzyme.

TABLE II



Latex. (N_2 content 0.11%)

Wet coagulum 67 parts, by weight, N_2 0.15%

Pressed

Wet coagulum remaining 50 parts N_2 0.26% which is equivalent to 0.78% N_2 on dry rubber present.

Hand rolled after standing six weeks to 19.1 parts containing 0.20% N_2 or an equivalent of 0.23% N_2 on the dry rubber present.

Washed, creped and dried gave 16.4 parts of dry rubber containing 0.19% N_2; the loss here was probably mechanical due to the removal of the surface scale which had formed and which was high in proteins.

Serum pressed out 17 parts—S. G. 1.011 N_2 0.07%

Serum 33 parts (S. G. 1.009) N_2 0.06%

Held for 14 days with no evaporation N_2 0.04%

Held for 60 days with no evaporation N_2 0.03%

No further loss in N_2.

Eaton and Grantham carried out a series of experiments along this line and came to the following conclusions (*Agricultural Bulletin,* Federated Malay States, Nov., 1915):

(1) That this natural coagulation of the latex of Hevea braziliensis is due to certain bacteria which infect the latex after coagulation.

(2) That these are two distinct types of organisms, one favored by aerobic conditions, which tend to inhibit coagulation, and the other favored by anaerobic conditions, which affect coagulation of the latex.

(3) That the coagulation of the latex under anaerobic conditions is not constant, on some days complete coagulation occurring and on others much less complete. This is possibly due to a variation in the constituents of the latex.

(4) That by the addition of various sugars, coagulation under both conditions always occurs and is due in their opinion to the fact that a medium is formed more favorable for the organisms, which produce coagulation, and less favorable to those producing putrefactive changes.

In a previous article by these men they called attention to the fact that an excess of acetic acid in coagulation retards the rate of cure and upon biological grounds it is explained that the micro-organisms which produce accelerating substances are killed. To investigate this point, some rubber was coagulated with acid and then soaked in alkaline solutions, thus producing a more favorable medium for biological changes to occur. Slab rubber was the form chosen with which to carry out the test. The results were that the rubber cured in about one half the normal time. Whether this is to be explained upon purely a chemical or biological basis remains for further research, which has been attempted at a more recent date.

If the preceding assumptions are

correct that there exists in the rubber some substance which has the power of decomposing into accelerating compounds, the question arises, What is the period during which the change in the raw rubber causing acceleration of rate of cure takes place?

To answer this question, the two experimenters, above referred to, coagulated some latex, then from the coagulum removed a sample creped, dried it in a hot air drier and then blocked it on the same day as coagulated. The next day a new sample was taken from the original coagulum and treated in the same manner; the following day another sample, and so on until they had ten samples taken in as many days. These were then milled up and cured, tested, and the following conclusions were drawn:

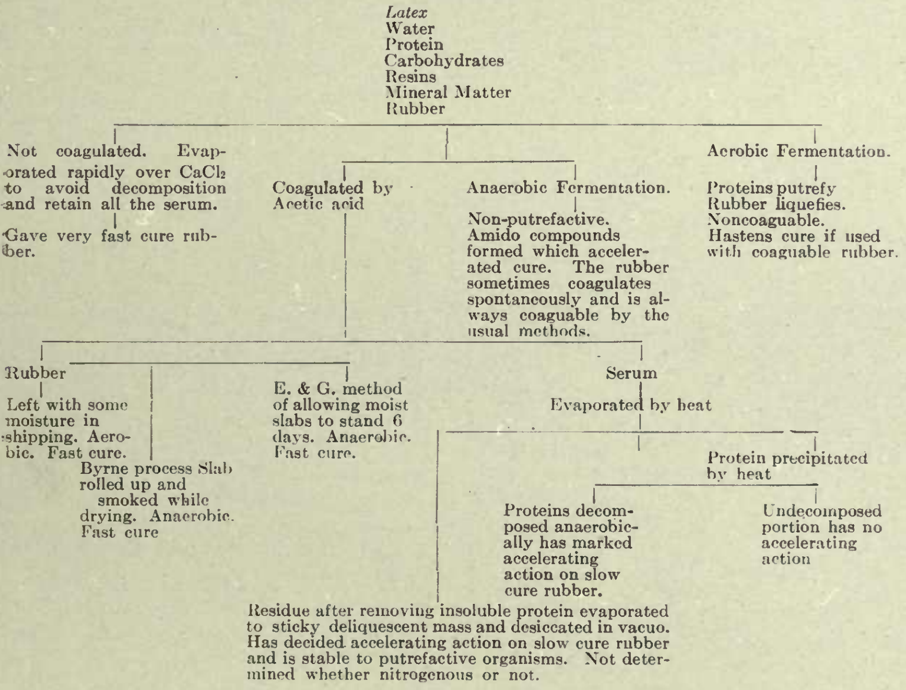
(1) That the rate of cure increases until the sixth day and then remains practically constant.

(2) That the greatest change occurs in the first three days. It is perfectly safe, however, to crepe the rubber after the tenth day and it will remain constant after that time. Even samples that have been aged seem to retain their accelerating bodies.

In the above, attention was called to the remarkable accelerating action which alkalis have upon rate of cure and it was suggested that this might be due either to a biological effect or to a purely chemical one. Eaton investigated this point in the following manner:

Samples of both fast curing and slow curing rubbers were taken and soaked in dilute alkaline and acid solutions for twenty-four hours, then milled, cured and tested, comparison being made in each case against a control sample.

TABLE III



Latex
Water
Protein
Carbohydrates
Resins
Mineral Matter
Rubber

Not coagulated. Evaporated rapidly over $CaCl_2$ to avoid decomposition and retain all the serum.

Gave very fast cure rubber.

Coagulated by Acetic acid

Anaerobic Fermentation.

Non-putrefactive. Amido compounds formed which accelerated cure. The rubber sometimes coagulates spontaneously and is always coagulable by the usual methods.

Aerobic Fermentation.

Proteins putrefy Rubber liquefies. Noncoaguable. Hastens cure if used with coaguable rubber.

Rubber

Left with some moisture in shipping. Aerobic. Fast cure.

Byrne process Slab rolled up and smoked while drying. Anaerobic. Fast cure

E. & G. method of allowing moist slabs to stand 6 days. Anaerobic. Fast cure.

Serum

Evaporated by heat

Protein precipitated by heat

Proteins decomposed anaerobically has marked accelerating action on slow cure rubber.

Undecomposed portion has no accelerating action

Residue after removing insoluble protein evaporated to sticky deliquescent mass and desiccated in vacuo. Has decided accelerating action on slow cure rubber and is stable to putrefactive organisms. Not determined whether nitrogenous or not.

It was found that the alkalis had a marked accelerating action upon the rate of cure, which was apparent in both the fast and slow curing rubbers, while acid had a pronounced retarding effect. These tests were carried out with finished dried crepes so that the biological effect was eliminated and thus the chemical action made more certain. However, the way in which this chemical effect takes place is not known. The evidence seems to point to the action of the alkali upon certain constituents in the rubber. The retarding effect of mineral acids is especially noted with quantities beyond the minimum required for coagulation; therefore, the serious question of trying to substitute sulphuric acid in the place of acetic as now used.

Attention has also been called to the fact that rubbers which have been treated with alkalis do not show good tests upon ageing.

Let us hope that more work along this line will follow and that better methods of coagulation will be found, thus producing more uniform rubber from the manufacturer's viewpoint.

CHAPTER IX

Theory of the Constitution of Rubber

To determine the true constitution of caoutchouc is no easy matter, as will be seen from what follows. In the first place, we must be certain that we have obtained a pure sample with which to work. The fact that it belongs in that class of compounds which occur in the realm of colloidal chemistry does not simplify our task to any great extent.

It has no definite melting point, no solution from which it may be crystallized. Ozone does form with caoutchouc an ozonide which is capable of being purified and studied. It was by means of this that Harries came to the conclusion that there existed a slight chemical difference in the constitution of Congo caoutchouc and Para. (*Annalen,* 1913, 395, 211.) For some time caoutchouc has been given the formula of $C_5 H_8$ and then on account of its analogy to the terpenes it is written $C_{10} H_{16}$ or some multiple of this. Faraday and Berzelius were in possession of this knowledge.

The first important work along this line was done by Gladstone and Hibbert. (*Trans. Chem. Soc.*, 1888, 53, 679.) They tried to obtain pure rubber by dissolving it in chloroform and then precipitating it with alcohol. Even this method seems to give a sample which contains some oxygen.

They found upon analysis of a sample prepared as stated above that it contained $C = 87.46$ and $H = 12.00$. They calculated upon the basis of $C = 88.24$ and $H = 11.7$ the formula C_5H_8.

We are fortunate, however, in having more evidence as to its formula than that of analysis alone. The usual methods of determining molecular weights, of course, cannot be applied here, colloidal solutions showing very little if any osmotic pressure and not obeying the freezing point and boiling point laws of Roult.

Bary and Weidert (*Compt. Rend.* 1912, 154, 1159) assumed that the molecule of caoutchouc was made up of several nuclei of five or ten carbon atoms each. Then they tried to explain that the vulcanization consisted in the union of an atom of sulphur to each end of a chain of $C_{10}H_{16}$ complexes.

If this is true, then the $(C_{10}H_{16})_n$ has a value of nearly 2500, which makes the molecule appear to be a very large one. It is also apparent that if we continue to vulcanize and go on toward ebonite, before that is possible, there must be a breaking down of this large molecule that more sulphur may add itself; or, in other words, depolymerization must take place.

It does not seem necessary to hold that the caoutchouc molecule is a large one. We have two derivatives whose molecular weights have been determined, the ozonide and nitrosites, and these point to a carbon content of ten and twenty atoms.

Some day we hope to find a solvent which will resolve the colloidal aggregation of a rubber solution into a true solution and thus make the direct determination of its molecular weight possible.

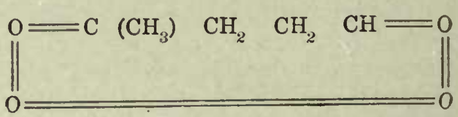
We know that by certain manipulations we are able to change the aggregations in colloids and thus produce substances of different properties. This Harries did in the case of caoutchouc (*Annalen,* 1911, 383, 157) and he obtained three materials which he designated as *a*, *b* and *c*.

The *a* material is obtained by precipitation with alcohol. The *b* is insoluble and is formed when *a* is allowed to stand. The *c* is an oil obtained from *a* by maintaining a temperature a little above normal. It has been suggested that the caoutchouc exists in the latex in the *c* modification which is soluble in ether. Harries extracted some from the latex with ether and, upon standing, this changed over into rubber. Weber had observed this and put forth the idea that this substance was a dipentene $C_{20}H_{32}$ in the latex surrounded by a protein which acted as a protective colloid. Therefore, when the coagulation reagent is added, this protein is removed and at the same time the dipentene is polymerized, for it becomes insoluble. Henrichsen and Kindscher (*Ber.* 1909, 42, 4329) determined the molecular weight of the hydrocarbon from the latex by extracting it with benzine and determining the lowering of its freezing point. This gave a molecular weight of over 3000, and they felt certain that the rubber existed in a colloidal state and that it was not a dipentene. In 1860. Greville Williams distilled some rubber at as low a temperature as possible and, upon refractioning, obtained two samples with boiling points between 37-40 degs. and 170-180 degs., respectively. The first portion was mostly isoprene and the latter was caoutchine, possessing twice the vapor density of isoprene. Bouchardat (*Compt. rend.*, 1879, 89. 361 and 1117) found that isoprene changed, when allowed to remain in a sealed tube, to a substance having a different odor. Then Wallach (*Annalen,* 1884, 255, 311; 1885, 227, 292; 1887, 238, 88) pointed out that this substance was identical with caoutchine and dipentene. Then Tilden found that dipentene decomposes into isoprene and this has been found by Wallach to change into caoutchouc.

Thus we may get the relations of these substances as follows: Caoutchouc by heat changes into isoprene and dipentene; dipentene in a red hot tube changes to isoprene; isoprene spontaneously changes into caoutchouc; in a sealed tube, however, isoprene goes into dipentene. Other fractions have been obtained and studied, but few conclusions have been drawn from that source.

We know that caoutchouc is an unsaturated hydrocarbon, but the exact degree of this unsaturation has been a subject of dispute. For instance, Gladstone and Hibbard (*Trans. Chem. Soc.,* 1885. 53, 679) described a chloride of the formula $C_{10}H_{14}Cl_8$, which is best explained by assuming the addition of six atoms of chlorine thus indicating these ethylene groups.

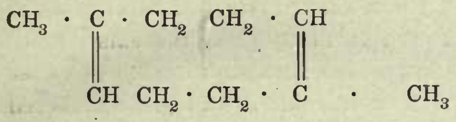
Harries then tried the action of ozone upon a chloroform solution of purified Para rubber and obtained a compound giving a molecular weight according to the formula $C_{10}H_{16}O_6$. By a previous experiment, it was found that in ozonides we have three atoms of oxygen associated with each ethylene group, therefore we must have here two such linkages for each ten carbon atoms. Harries also produced a diozonide of the formula $C_{10}H_{16}O_8$. When this was hydrolyzed there resulted hydrogen peroxide, a keto- or di-aldehyde, lævulinic acid, and also another acid. To explain this, he assumed that the caoutchouc molecule may be represented by an open chain formula. He later found that this was not true, but that the primary products of hydrolysis were lævulinic aldehyde and the peroxide of lævulinic aldehyde:



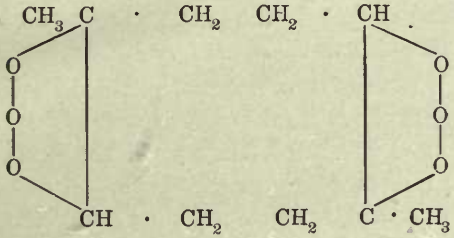
Further hydrolysis of this decomposes it into lævulinic acid and hydrogen peroxide.

To account for these two primary products of hydrolysis from the diozonide and the presence of two double bonds to each ten carbon atoms requires that the molecule be regarded as a cyclic one, because if it were an open chain it would give two hydrolysis products oxygenated at only one end of their chains.

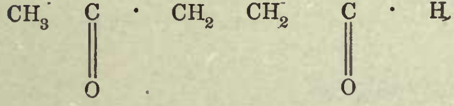
Thus Harries suggested that the constitution of caoutchouc was represented by the formula of a 1:5 dimethylclyclooctadiene:



Its ozonide is then:

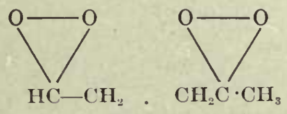


Its aldehyde:



$$CH_3\cdot\underset{\substack{\| \\ O}}{C}\cdot CH_2\ CH_2\ \underset{\substack{\| \\ O}}{C}\cdot H$$

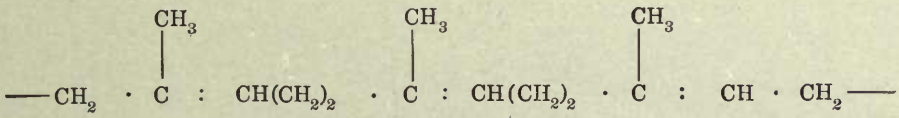
Its aldehyde peroxide:



Here Harries suggested that polymerization took place due to unsatisfied partial valences which, according to Thiele's theory, is possible where we have double bonds in octadiene ring formation, and thus an indefinite number might be linked together.

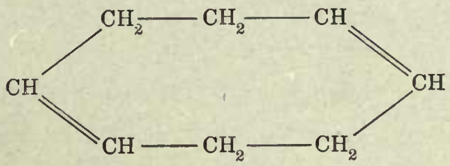
Pickles (*Trans. Chem. Soc.* 1910, 97, 1085) criticises this theory by calling attention to the fact that if this were true, the new polymeride should possess a less degree of unsaturation than the simple substance, and this is not the case. The tetrabromide is also formed without any depolymerization and yet we have four bromine atoms to each ten carbon atoms.

He also points out that under destructive distillation, we should expect to get dimethylclyclooctadiene and this is not the case; and yet even under reduced pressure we never get a substance containing less than twenty carbon atoms. Pickles chose to assign a chain formula made up of C_5H_8 nuclei:

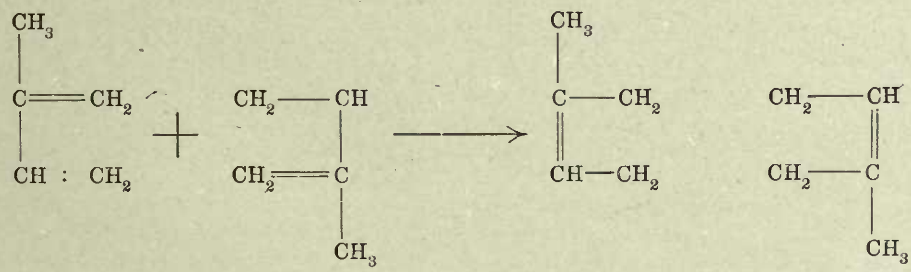


$$—CH_2\cdot\overset{\substack{CH_3\\|}}{C}:CH(CH_2)_2\cdot\overset{\substack{CH_3\\|}}{C}:CH(CH_2)_2\cdot\overset{\substack{CH_3\\|}}{C}:CH\cdot CH_2—$$

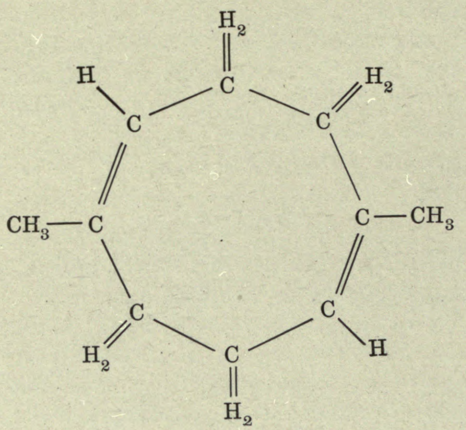
From the study of its oxidation products, we see that the ends of this chain must be linked together. However, the greater amount of favor rests on the side of the eight membered ring. Willstatter (*Ber.*, 1905, 38, 1975) was able to prepare clyclooctadiene and this he was able to polymerize to form diclyclooctadiene:



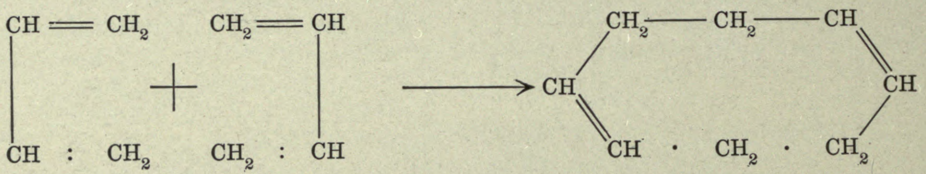
If isoprene may be made to condense and form dimethylclyclooctadiene:



Showing it in ring form:



then it follows that butadiene should yield clyclooctadiene:



When Harries compared the ozonides of butadiene, caoutchouc and clyclooctadiene when hydrolyzed, he found them to yield the same products. This furnishes us the evidence that caoutchouc is an eight membered ring, and from what has been said above it does not seem necessary to assume that the molecule is any larger than $C_{10}H_{16}$.

When the ozonides of purified Para and of artificial isoprene caoutchoucs are hydrolyzed, they yield the same products and thus the conclusion that the wild caoutchouc must have the constitution of the polymerized isoprene.

CHAPTER X

Synthetic Caoutchouc

The question of being able to produce artificial rubber is one that has interested a great many workmen and especially has it been of great interest to the laymen of the rubber industry. I once heard the superintendent of a large rubber factory say, when asked his opinion as to the possibility of synthetic rubber, that he expected to see " synthetic apples " first.

Several years ago, certain men and in fact we might say certain nations began to appreciate the fact that the time was approaching when the amount of wild rubber then being produced would not be sufficient to supply the world's demands. To meet this condition, Mons. E. Coustet proposed three solutions:

First, he said we must use the mineral caoutchouc which had been discovered in the Castleton mines, England, in 1785, and later in France in 1816, and still later in the United States.

Second, we must employ an artificial product possessing the properties of the natural product. In 1846, Sacc and Jonas produced such a substance by treating linseed oil with azotic acid. Another similar substance had been produced by treating oil of turpentine with sulphuric acid.

The third suggestion was to increase the supply of natural product, but this seemed like a very slow method.

The first of these suggestions has been utilized and in addition to these mineral rubbers we are using today large quantities of synthetic mineral rubber.

The third way of course has proved the method which has largely solved our problem to date, for the quantity of the natural product has been increased both by obtaining more of the wild rubber and by the great development of plantations.

The second idea, that of artificial rubber, however, still remains the dream of the chemist. It is not a question of merely producing it, for that has been accomplished, but of producing it upon a commercial basis.

How great the demand has been for the artificial product is reflected in the following statement found in the *Independent* (Sept. 13, 1906, 61:648-9): "If any ambitious young man would like to earn $10,000,000 next year he has the chance. The world will gladly pay him that, or even more if he will show how to make India rubber cheaply. He will find much of the preliminary work already done; only one link is lacking in the chemical process. All he has to do is to reverse a well known chemical reaction. Any freshman chemist can do it—on paper. This is all there is to it:

$$2C_5H_8 \longrightarrow C_{10}H_{16}$$ "

We know that isoprene results from the distillation of caoutchouc. In 1860, Greville Williams isolated isoprene with the apparent formula of C_5H_8 (*Proc. Roy. Soc.* 1860, 10, 516); therefore, the above is possible and has been accomplished, but not on a commercial basis. Bouchardat in 1875 (*Compt. rend.* 1875, 80, 1446) had observed that some of the distillation products of caoutchouc could be changed into rubber when treated with hydrochloric acid in the cold. This substance was undoubtedly isoprene. He also called attention to a polymer of this having the formula $C_{10}H_{16}$.

Isoprene may be made from turpentine. In 1882, Sir William Tilden (*Trans. Chem. Soc.* 1884, 45, 411) observed that isoprene could be made from terpenes (substances obtained from oil of turpentine). He also observed that this isoprene upon long standing polymerized into rubber. Attempts were then made to hasten this reaction. Tilden made his isoprene by passing oil of turpentine through pipes heated to a red glow. If the isoprene may be cheaply converted into caoutchouc, then the raw rubber industry may be transferred from the rubber tree of the tropics to the pine trees of our own country.

A British patent of 1907, proposed by Heinemann, describes the process of making synthetic rubber by heating a mixture of acetylene and ethylene at a dull red heat and there results divinyl,

$$CH_2 = CH \cdot CH = CH_2$$

then by the ordinary reaction using methylchloride, this is converted into methyl divinyl, or isoprene,

$$CH_2 = C \cdot CH_3 \cdot CH = CH_2$$

Again the isoprene is made to polymerize into caoutchouc.

There was a time when the " synthetic rubber scare " nearly produced a panic in the rubber plantation securities. This furnishes evidence of the almost unreasonable fluctuation of a stock market.

Harries in 1905 had established, he thought, the chemical constitution of caoutchouc to be 1.5 dimethylcyclooctadiene and this aided the problem of building up the synthetic product (*Ber.* 1904, vol. 37, p. 2708; 1905, vol. 38, p. 1195).

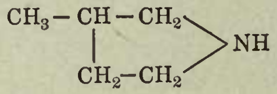
In 1910, Harries reported in a lecture given in Vienna that he had succeeded in converting isoprene into caoutchouc by heating it in sealed tubes in the presence of glacial actetic acid, and he deserves the credit of being the first man to publish a method for this which could be repeated by another investigator. Harries, in 1911, found that isoprene in the presence of metallic sodium polymerized very rapidly, but that the product was different from the one obtained where heat was used. (*Annalen,* 1911, vol. 383, p. 188).

In 1884, Tilden also suggested that it was possible to polymerize the homologues of isoprene and in so doing to obtain substances varying from resinous bodies up to those possessing the properties of rubber. This of course suggested new materials as starting products in the procuring of synthetic caoutchouc.

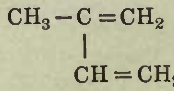
O. Wallach (*Annalen,* 1884, 225, 311; 1885, 227, 292; 1887, 238, 88) studied the behavior of isoprene and did succeed in polymerizing it by means of the action of light.

Weber repeated the work of Tilden and reports that he obtained 211 grams of caoutchouc from 300 grams of isoprene, after keeping it for nine months.

In all this work, it will be observed that the isoprene has been obtained from some other natural source, but in 1897 Euler was able to synthesize this substance. (*Ber.* 1897, 30, 1989; *J. Prakt. Chem.* 1898, 57, 131). He began with β-methyl pyrrolidine



and by successive treatment with CH_3I and KOH was able to produce isoprene:



$$CH_3 - \underset{\underset{\displaystyle CH = CH_2}{|}}{C} = CH_2$$

It is apparent, therefore, that the product which results depends upon the method used and also upon the material used in starting, as is shown by the statements of Holt in *Z. angew. Chem.* 1914, vol. 27, p. 153.

Caoutchoucs from Butadiene, C_4H_6

Normal caoutchouc: (by heating), easily soluble, elastic, vulcanizable.

Carbon dioxide caoutchouc: Insoluble, does not swell up, moderately elastic, unvulcanizable.

Sodium caoutchouc: Easily soluble, elastic, vulcanizable.

Caoutchoucs from Isoprene, C_5H_8

Normal caoutchouc: Easily soluble, elastic, vulcanizable.

Carbon dioxide caoutchouc: Insoluble, does not swell up, elastic, vulcanizable.

Sodium caoutchouc: Easily soluble, not elastic, difficultly and incompletely vulcanizable.

Caoutchoucs from Dimethylbutadiene, C_6H_{10}.

Normal caoutchouc: Easily soluble, not elastic, can only be vulcanized to hard rubber.

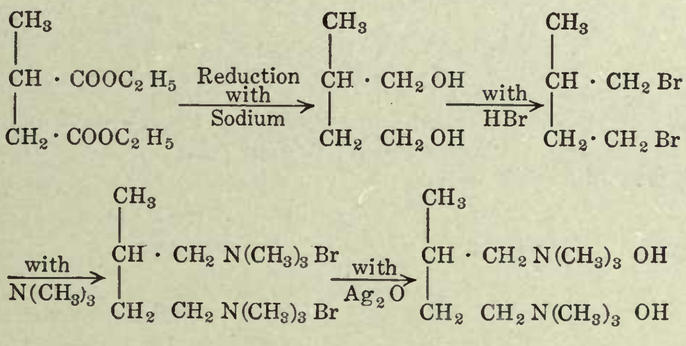
Carbon dioxide caoutchouc: Insoluble, does not swell up, not elastic, difficultly vulcanizable, easily oxidizable.

Sodium caoutchouc: Soluble and insoluble modifications, not elastic, unvulcanizable.

From the above table, it may be seen that by properly choosing the material to start with, and by use of the proper process of polymerization, it is possible to obtain caoutchouc with entirely different properties. This has a suggestion in it of technical importance for it points out the fact that some day we may be able to produce and emphasize any particular property that is desired.

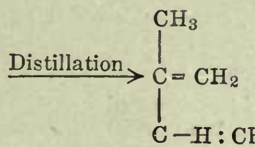
The first thing to be accomplished is the production of isoprene or its homologues, then a method of polymerizing these substances. Both of these processes must be such as can be worked on a commercial basis and must produce a final product with chemical and physical properties analogous to the native rubber and at a cost to compete with the native rubber.

We shall now consider different means of producing isoprene. It was noted above that Tilden obtained about a five per cent yield of isoprene from turpentine, but even though a good yield could be obtained, the supply of turpentine is very variable and uncertain. Several men have carried out valuable investigations along this line. Neresheimer (*Inaug. Dissert. Kiel,* 1911) began with the diethyl ester of pyrotartaric acid, which he reduced by means of sodium and then the following steps as indicated here:



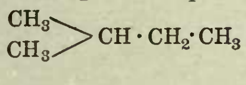
$$\begin{array}{l}CH_3\\ |\\ CH\cdot COOC_2H_5\\ |\\ CH_2\cdot COOC_2H_5\end{array}\xrightarrow[\text{Sodium}]{\text{Reduction with}}\begin{array}{l}CH_3\\ |\\ CH\cdot CH_2OH\\ |\\ CH_2\quad CH_2OH\end{array}\xrightarrow[\text{HBr}]{\text{with}}\begin{array}{l}CH_3\\ |\\ CH\cdot CH_2Br\\ |\\ CH_2\cdot CH_2Br\end{array}$$

$$\xrightarrow[N(CH_3)_3]{\text{with}}\begin{array}{l}CH_3\\ |\\ CH\cdot CH_2N(CH_3)_3Br\\ |\\ CH_2\quad CH_2N(CH_3)_3Br\end{array}\xrightarrow[Ag_2O]{\text{with}}\begin{array}{l}CH_3\\ |\\ CH\cdot CH_2N(CH_3)_3\ OH\\ |\\ CH_2\quad CH_2N(CH_3)_3\ OH\end{array}$$



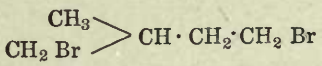
$$\xrightarrow{\text{Distillation}}\begin{array}{l}CH_3\\ |\\ C=CH_2\\ |\\ C-H:CH_2\end{array}$$

This method has the great advantage of producing a pure product. Matthews and Strange (*English Pat.* 4189, 1910) worked out a different method starting with isopentane,



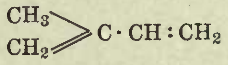
$$\begin{array}{l}CH_3\\ CH_3\end{array}\!\!>CH\cdot CH_2\cdot CH_3$$

first converting it into the dihalogen compound,



$$\begin{array}{l}CH_3\\ CH_2Br\end{array}\!\!>CH\cdot CH_2\cdot CH_2Br$$

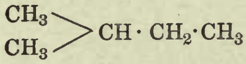
From this the halogen acid is then removed and isoprene results:



$$\begin{array}{l}CH_3\\ CH_2\end{array}\!\!\geqslant C\cdot CH:CH_2$$

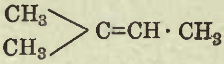
Then later we find another process beginning with the same substance when the Badischer Anilin und Soda

Fabrik (*Fren. Pat.* 43512, 1911) obtained isoprene by the following steps:

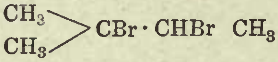


is converted into the monohalogen,

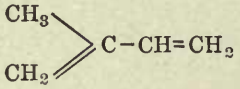
this when treated with lime yields



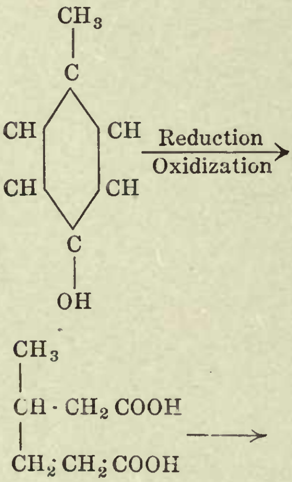
trimethylethylene. This is then converted into the dihalogen derivative,



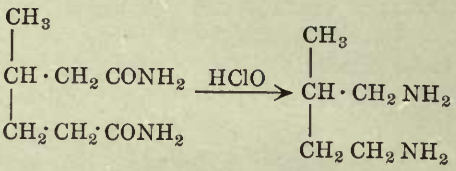
and when this is passed over a catalytic agent under reduced pressure at a temperature of 350 deg., isoprene results,



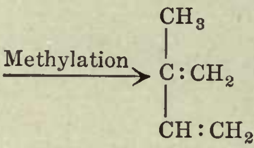
The Bayer Co. next produced isoprene, beginning with a coal tar product. They used p-cresol which is first reduced and then oxidized and this treatment will break the ring structure. The steps are indicated as follows:



$$\begin{array}{l}CH_3\\ |\\ CH\cdot CH_2COOH\\ |\\ CH_2\cdot CH_2\cdot COOH\end{array}\longrightarrow$$



$$\begin{array}{l}CH_3\\ |\\ CH\cdot CH_2\,CONH_2\\ |\\ CH_2\cdot CH_2\cdot CONH_2\end{array}\xrightarrow{HClO}\begin{array}{l}CH_3\\ |\\ CH\cdot CH_2\,NH_2\\ |\\ CH_2\,CH_2\,NH_2\end{array}$$



$$\xrightarrow{\text{Methylation}}\begin{array}{l}CH_3\\ |\\ C:CH_2\\ |\\ CH:CH_2\end{array}$$ is isoprene.

Heinemann (*Eng. Pat.* 13252, 1908) proposed that by the hydrolysis of starch, then oxidization and treatment with phosphorus trisulphide, there would result methylthiophene which upon reduction would give isoprene. This is the method which gained wide newspaper publicity for it suggests the production of auto tires out of potatoes.

Harries (*Annalen,* 1911, 383, 157) worked out a method starting with alcohol, the necessary steps of which method are indicated here:

$$CH_3\,CH_2\,OH\longrightarrow CH_3\,COOH\longrightarrow CH_3\,COCH_3$$
$$\longrightarrow (CH_3)_2\cdot C\,(C_2H_5)\,OH\longrightarrow CH_3\cdot CH:C:(CH_3)_2$$
$$\longrightarrow CH_3\,CHBr\,CBr\,(CH_3)_2\longrightarrow CH_2:CH-C\begin{smallmatrix}CH_3\\ CH_2\end{smallmatrix}$$

This method becomes a possibility inasmuch as commercial alcohol is now available. It is claimed for this process that it will yield from 60 to 75 per cent pure isoprene.

Matthews and Strange (*Eng. Pat.* 4572, 1910) then carried out some work with the amyl alcohols, both the iso and active, found in fusel oil. By carefully chlorinating these substances, passing the products over soda lime heated to 470 deg. and then fractionating, they claimed to have obtained a forty per cent yield of isoprene.

This constitutes a brief survey of the attempts which have been made to produce isoprene, the substance which by polymerization we are able to convert into caoutchouc.

Next in order, therefore, we must consider the ways which we have for effecting this latter change.

Some of these have already been mentioned, for example, its treatment with acid, autopolymerization, light, etc., all of these processes being slow and producing uncertain results. It was to hasten this process that heating in sealed tubes and then treatment with acetic acid was tried. From the use of these substances to accelerate the change, we find almost every class of compounds, both organic and inorganic, being used, even down to the Röentgen rays.

The caoutchoucs prepared by the above reagents will respond to tests, which Harries laid down for a true caoutchouc and thus these are called "normal caoutchoucs."

Then Harries and Matthews independently found that sodium or even amalgams, either hot or cold, would polymerize isoprene either in the cold or with a little heat, and effect this change almost quantitatively. This final product does not yield the same ozonide as the normal caoutchouc, indicating that it must possess a different constitution. As stated in the beginning, Tilden suggested that it was possible to produce caoutchouc from the homologues of isoprene; also, therefore, we shall discuss briefly the one most commonly used and the one which has given the best results, namely, Butadiene. Harries started with ethylmethylketone and reduced it to sec-butyl alcohol, which may be dehydrated, then by producing the dibromide and treating this with soda lime, butadiene results.

Hexahydrophenol has been converted into butadiene by heating it to a temperature of 600 deg. C.

It was observed by Ehrlich in 1905 that the addition of amino acids would increase the production of higher alcohols in fusel oil during fermentation. With this idea,, Fernbach and Strange worked out a cheap method of producing butyl alcohol and acetone. This alcohol is then converted into the chloride, and then by chlorination into the dichloride, which when heated with soda lime will produce butadiene,

$$CH_3\ CH_2\ CH_2\ CH_2\ OH \longrightarrow$$
$$CH_3\ CH_2\ CH_2\ CH_2\ Cl \longrightarrow$$
$$\left.\begin{array}{l} CH_3\ CH_2\ CHCl\ CH_2\ Cl \text{ or} \\ CH_3\ CHCl\ \ CH_2\ CH_2\ Cl \text{ or} \\ CH_2\ Cl\ \ CH_2\ CH_2\ CH_2\ Cl \end{array}\right\} \begin{array}{l} \longrightarrow \\ \longrightarrow CH_2{=}CH-CH{=}CH_2 \\ \longrightarrow \end{array}$$

The Synthetic Products Co. succeeded in converting butyl aldehyde into the aldol, and this when reduced gives the 1,3-butyleneglycol; this is converted into the dichloride, and when treated with soda lime butadiene results.

$$CH_3\ CHOH\ CH_2\ CHO \longrightarrow CH_3\ CHOHCH_2\ CH_2\ OH \longrightarrow$$
$$CH_3\ CHCl\ CH_2\ CH_2Cl \longrightarrow \underset{\text{Butadiene}}{CH_2{=}CH \cdot CH{=}CH_2}$$

Several other methods have been used to produce this substance, and in fact several other homologues have been produced. The methods used to polymerize butadiene are similar to the ones used upon isoprene. The sodium butadiene seems to be the best, however. The polymerization is complete in about three hours if it is held at a temperature of from forty to fifty degrees.

This constitutes a brief survey of the synthetic rubber industry up to date. Although it is very promising from the standpoint of the work which has been done, yet a great deal more remains to be done before the natural rubber securities need be disturbed again either in the United States or in Europe.

CHAPTER XI

Chemical and Physical Testing of Crude Rubber

As in the analysis of every substance, so in the analysis of crude rubber, the chemist must first obtain what may be regarded as a uniform sample. This, at first thought, seems a very simple matter, and yet it is one that causes as much if not more trouble than any other step in the complete analysis of any substance.

It is obvious that the analysis of a few ounces of rubber is absolutely worthless unless the sample is truly representative of the entire lot whose composition is desired. Therefore, a few general directions are necessary for the obtaining of what may be regarded as uniform a test lot as possible.

Rubber comes into the market in extremely varying forms and lots. Of course, the more uniform the rubber the easier it is to obtain a good sample and vice versa. The plantation rubber is comparatively easy to sample. It will be remembered that the rubber comes into the market in the form of sheets, blocks or slabs, balls, spindles, thimbles, twists, sausages, scraps of every size and shape, biscuits, etc. Some shipments are small, others are large; some of the above forms are small and some large. It naturally follows, of course, that the smaller the forms and the smaller the shipments, the easier the task of sampling.

As an example, let us select a sample from a large shipment made up of many containers of which the forms are rather large. Enough of the containers should be opened and thoroughly inspected to learn whether it may be regarded as a uniform shipment, that is, whether each package is a representative sample of the whole. If this is true, then a sample need not be taken from each package, but only from every other one or every third one. This, of course, is to be judged from the general appearance of the lot. If the forms are also running large, samples may be cut from representative ones taken. This will keep the volume of the sample down and at the same time not impair its uniformity. When cutting a ball or slab, it must be cut completely through. Some take a slice diagonally through the form while others take one through the middle perpendicular to the long axis. Ordinarily, sampling is not pleasant work and is, therefore, sadly neglected. A sample is wanted, some inexperienced help is often sent to get it and he does so with the least possible expenditure of energy and thought. Too much emphasis cannot be placed upon this first and very important step in the analysis of rubber, or, in fact, any substance.

Washing Loss

The sample having been obtained, the first thing to be done is to determine what is called the "washing loss." This will include in its per cent that due to moisture, dirt, and the soluble non-rubbers, which include proteins and carbohydrates. To determine the washing loss, the larger the sample taken the better; therefore, this test is better carried out on a factory scale than in the laboratory. A batch of rubber is first of all subjected to the washing process, just what method to be used depending upon the grade of crude rubber. If it comes in large, somewhat hard forms, it may be softened first in warm water and then cut up into suitable sizes to pass through the washer. The rolls are set rather far apart at first and water plays over them. As the rubber passes between the rolls, it soon takes the crepe form and the washing continues until the impurities are all removed. The rolls are gradually brought closer together so that a thin crepe may be obtained, thus enabling the rubber to dry more quickly. The thickness of these sheets varies greatly in different factories. After this it is dried and the loss in weight which it suffers, calculated in per cent of the original batch, represents the " washing loss."

This is a test which has great influence in determining the value of wild rubbers. On account of the cleanly methods of handling, the plantation rubbers run the lowest in washing loss while some grades of African run over fifty per cent washing loss.

A list of the more common rubbers with their average results of analysis is given on another page. If the determination has to be carried out on a laboratory basis, great care must be exercised in selecting the sample, for misleading results may be obtained unless it is very carefully supervised.

From the analysis of crude rubber, not a great deal is to be gained. We shall present the tests ordinarily carried out in the order of their importance.

Determination of Moisture

First, the moisture present in rubber must be determined. Moisture may cause a great deal of trouble in different manufacturing processes and, therefore, before being used, the rubber must be thoroughly dried. This is a test which it is not necessary to carry out in the chemical laboratory very often, for a man with much experience in handling rubber is soon able to judge as to the amount of moisture present in a sample, or at least as to whether or not it is dry enough to be used in compounding. If it is imperative to carry out this test in order to trace some trouble, then the best method consists in heating five to ten grams of the sample, reduced to as small parts as possible, in a vacuum oven until it comes down to a constant weight. This will require only a short time with some rubbers and a comparatively long time with others. Sometimes we see this test being carried out in an ordinary hot-air oven. Comparative results may be obtained by this method, but it is not to be recommended. The best and most accurate method consists in allowing the rubber to stand over sulphuric acid in a vacuum dissicator at normal temperature.

The tendency of rubber to oxidize with elevation of temperature must be guarded against. The unvulcanized rubber is less susceptible to this influence than the vulvanized.

Theoretically, we want to dry the rubber in the shortest possible time at the lowest temperature possible. This, of course, is effected by drying in a vacuum, the temperature used being generally about 60 deg. C. If a hot-air oven must be used, 105-110 deg. C. is used. At this temperature and, in fact, at 60 deg. C., some rubbers running high in a flabby resin become very soft and tacky and it is hard to remove the last traces of moisture, likewise they are more apt to oxidize. To obviate the difficulty of oxidization, during the drying, Obach devised a method whereby he dried the rubber in a stream of dry carbon dioxide and then absorbed the moisture in a weighed U-tube containing sulphuric acid. This method determines the moisture directly, but is more or less difficult to control.

The percentage of moisture by whatever method determined, is calculated from the ratio of the loss during heating to the amount taken in the beginning. As a limit of water present in rubber for compounding, we may allow as high as 0.5 of a per cent. As before stated it is necessary only to perform this test occasionally to check up the efficiency of the drying system in use.

Estimation of Resin

The next determination is the one, which is no doubt carried out more than any other, namely, the estimation of the amount of resin. The principle, upon which this determination is based, consists in extracting a known weight of the washed and dried rubber with a solvent which will remove the resin. Acetone is the one used. The solvent is then evaporated in a weighed flask and the resin thus determined.

To actually carry out this test you should proceed as follows: A weighed amount of rubber, which has been washed and dried, is placed in an extractor, and here we might say that the form used depends on the wish of the operator. Many different forms are on the market. Of course, the Soxhlet form is good and has been and still is used a great deal. The Wiley extractor has been used with considerable success. The writer, however, at present is using the Bailey-Walker form and is well satisfied with its results. The great advantage in it comes in its compactness and the fact that the solution of the resin in acetone does not have to be transferred to a tared flask for weighing. The acetone used in these determinations should be freshly distilled off from potassium carbonate.

The larger the amount of rubber taken, the more accurate will be the result; therefore, let the size of the thimble in the extractor determine how much it is possible to take. The rubber is reduced to as small pieces as possible so that the maximum solvent action of the acetone will be had. Some rubbers when treated in this manner and then subjected to extraction, become very soft and tend to flow together, thus making complete extraction impossible. In cases of this kind, the rubber may be sheeted out as thin as possible on a mill. Then a weighed ribbon of this is rolled up in muslin and placed in the extraction thimble. The extraction is then begun by heating the acetone in the flask either over a water bath or electric hot plate and continued for a period of ten hours. This is ample time for the extraction if the sample has been properly prepared and the necessary precautions taken. The acetone is then evaporated off over a water bath and the flask is heated for three hours in an oven held at 105 to 100 deg. C.

One must be very careful as some resins are volatile at this temperature and thus a loss might be encountered. In fact, it was recently observed in our laboratory that there were present in some rubbers resin which would volatilize at just a few degrees above the boiling point of acetone. It is still an undecided question in the mind of the writer as to whether or not there are some which distill over with the acetone.

The percentage of resin is calculated on the basis of the rubber taken. The resin content varies within wide limits when we are considering all kinds of rubber, but varies within narrow limits for the same variety of rubber. For instance, Hevea will run about 3—4 per cent; plantation about 2—3 per cent, while Accra Lump will run from 30—40 per cent. The resins from South American rubbers are generally liquid and of a dark color. Plantation resins are also liquid, but of a lighter color. The African resins are generally yellow and more or less brittle, but soften with heat.

The amount of resin in a rubber is not an absolutely reliable criterion as to the value of rubber for manufacturing purposes. Ordinarily the low resin content rubbers are best for the resin may be considered really as a diluent.

Determination of Ash

The next determination of value is that of ash. The principle of this determination consists simply in incinerating a weighed amount of washed and dried rubber and thus obtaining the amount of mineral matter in the sample.

To carry out this test, as large a sample as possible is used and weighed into a large shallow formed crucible of known weight. Heat is very carefully applied and regulated so that the volatile substances will not take fire. Should this happen, they may be easily extinguished by superimposing the cover over the crucible. When the volatile products are removed. the heat is increased up to that of dull redness and held there until all carbonaceous material has disappeared. The weight of the residue is then obtained and its percentage calculated on the basis of the rubber taken.

The ash content of rubbers does not, or rather should not, vary within large limits. In fact, in the majority of rubbers, regardless of their source, the per cent should run from about 0.5 of one per cent up to 1.5 per cent. There are a few exceptions to this, however, and we find an ash as high as 3 per cent. The determination of the ash is of value for two reasons: First, it serves as a check upon the effectiveness of the washing process, for if it has been done hastily and incompletely, the ash will of necessity run high. Secondly, it serves as a means of detecting non-rubber materials. These determinations are the chemical tests most frequently carried out and the ones upon which the verdict of the investigator is largely based.

Determination of Nitrogen

Where a complete analysis is required, it becomes necessary to determine the proteids and other nitrogenous matter in the rubber. These cannot be determined directly, but we simply multiply the amount of nitrogen found by analysis by the factor 6.25. Not knowing the true nature of the rubber proteins, it is hardly necessary to say that this test does not furnish us with any reliable information. The test is carried out as follows: About two grams of rubber are weighed out and placed in a long-necked Kjeldahl flask, when 30 cc. of concentrated sulphuric acid and a drop of mercury are added. It is well to loosely cork the flask by putting a small funnel in the neck of the Kjeldahl. Heat is then applied to the flask, very carefully at first, until the first violent reaction has subsided. Then the heat is gradually increased until the acid boils quite vigorously. This is continued until the contents of the flask acquire a straw yellow color.

The solution is very cautiously diluted, and in some cases transferred into a larger flask, although the using of a large Kjeldahl in the beginning avoids this step. After dilution, one or two grams of sodium sulphide are added, then caustic soda, until the solution is distinctly alkaline. A few pieces of scrap zinc will prevent pounding when it comes to distillation.

The nitrogen of the original rubber has been converted into ammonium sulphate by the above treatment. Upon the solution having been made alkaline and upon the application of heat, ammonia will be distilled over into a known amount of N/5 sulphuric acid. When the ammonia is all driven over, the excess of acid is titrated back with N/5 alkali, using methyl orange as an indicator. From the amount of acid consumed during the distillation, the amount of nitrogen in the rubber taken is calculated and from this the protein. The nitrogen in some unwashed rubbers may run as high as one per cent. Of this considerable is due to albuminoids which are present in the rubber, but which are soluble and would be removed upon washing. It is the albuminoid nitrogen which undergoes putrefaction and imparts to the rubber a bad odor. It also has a deleterious effect on the rubber. This albuminoid nitrogen is sometimes determined by determining the difference between the nitrogen in the unwashed and washed rubber. A small percent of nitrogen in rubber is a sign of strength rather than of weakness in the rubber.

Determination of Insoluble Matter

The determination of insoluble matter is sometimes required. As the term implies, it includes those substances which are insoluble in the ordinary rubber solvents. Under insoluble matter, we find sand, clay, wood, humus, and other accidental impurities.

Theoretically it is an easy matter to treat a known amount of rubber with a solvent and weigh the residue, thus obtaining the insoluble matter, but the extreme viscosity of rubber solutions makes it a difficult matter to separate the insoluble from the soluble.

The methods employed give best results if the crude rubber is first milled when the pectus modification is broken down, and solution results more readily. A known amount of rubber is treated with either toluene or phenetol, the latter having been used by C. Beadle and H. P. Stevens. Even petroleum may be used and gives a solution, which may be filtered through a tared filter or centifuged and the residue determined.

Determination of Rubber

The insoluble matter as a rule runs a little lower than the ash as some of the inorganic matter exists as salts which are soluble in the solvents used. The determination of rubber proper, or the pure hydrocarbon, is generally obtained by difference, that is, the combined percentage of moisture, ash, organic protein, and acetone extract subtracted from 100. It may be determined directly, however. One or two grams of rubber are put into solution as indicated under insoluble matter and then allowed to settle of its own accord, or is hastened by centrifugal force. It is diluted up to 100 cc. and then 50 cc. are pipetted off and dropped into 100 cc. of warm alcohol, when the pure hydrocarbon is precipitated. To purify it the caoutchouc is precipitated several times, then dried in a weighed disk in a vacuum and its weight determined.

Instead of precipitating the rubber from the 50 cc. of solution it might have been transferred to a weighed flask, and the solvent evaporated off. The resin can then be removed by repeated washing with boiling alcohol under a reflux condenser. It may then be dried and its weight ascertained. The higher the resin content, the less accurate are both of these methods.

Its determination by formation of the tetrabromide has been outlined by Spence and Galletly. They first dissolved a small amount of rubber in carbon tetrachloride. To this they added a reagent composed of 6 cc. of bromine and one gram of iodine in one liter of carbon tetrachloride, and allowed to remain about six hours. When this solution is added to alcohol, the tetrabromide is precipitated. It may be purified by dissolving it in carbon disulphide and reprecipitating it with petroleum ether. This may be repeated if necessary. The pure tetrabromide is then fused with a mixture of sodium carbonate and potassium nitrate. The residue is taken up in a small amount of water, nitric acid added, boiled and the silver halide determined. From this the amount of rubber proper is calculated. A great deal has been published concerning this method and it has its merits in principle at least, but in the hands of the writer, it has never given concordant results.

Viscosity of Rubber

Schidrowitz and Goldsbrough (*J.S.C.I.*, 1909, p. 3) have called attention to some very interesting results from experiments upon the viscosity of rubber and its solutions. They point out that as is known, the viscosity of a liquid or of a solid contained in a liquid depends upon the state of aggregation of the molecules or physical aggregation. Therefore, the viscosity of rubber solutions should throw some light upon the chemical or physical state of aggregation in the rubber solution and this should give some idea as to the " nerve " of the rubber under consideration. The results of this work lead Schidrowitz to conclude that " Within the same species, viscosity measurements give a direct line as to strength and vulcanizing capacity. Comparing species with species, this does not hold good directly, probably because different species possess differently constituted molecules, and the relationship is, therefore, of a more complex order than between different specimens of the same species. At the same time the broad proposition holds good for all species, compared *inter se* or otherwise, that high viscosity figures indicate strength and low viscosity figures, weakness."

Specific Gravity

Specific gravity is sometimes determined, any one of the general methods for such work being employed. The information to be gained from this determination does not influence the judgment of the investigator to any extent. Only on rare occasions is it carried out on crude rubber, but it is used a great deal on vulcanized goods.

Sun Cracking

Another test, which has been suggested to be used upon both crude and vulcanized rubber, is known as the effect of " sun cracking."

To test the liability of rubber to sun crack requires a long period of time, and that, of course, renders the test almost useless because we do not have time to waste in waiting for a test that consumes a large amount of time. However, to obtain a test, which will show this property of the rubber, several artificial methods have been recommended. Weber subjected weighed samples of rubber, presenting the same area, to the action of acetone peroxide for two days. The samples were then removed, dried, weighed, and the increase in weight was to be considered as a measure of the liability of the rubber to sun crack. He claims that the results obtained were in agreement with the actual results obtained by carrying out the sun-cracking test.

Ditmar tried to obtain a set of comparative results illustrating the same property of rubber. He placed in glass tubes weighed samples of rubber, then passed oxygen into these until the air was all excluded, when the tubes were sealed. These were then heated in a Carius furnace for from five to twenty hours at a temperature of 100 deg. C. The samples of rubber were then removed and weighed and their increase in weight he hoped to be a measure of the liability of the rubber to sun crack. He later modified his test by placing the rubber in a tube supplied with ground valves at each end and he maintained a constant temperature by lowering this tube into boiling water. Whether the results obtained are of much value is a question.

Vulcanizing Test

After all of these tests have been outlined and after a sample has been subjected to all of them, the question which would still remain unanswered is the one, which is perhaps oftenest asked by the manufacturer: How will the rubber conduct itself during vulcanization? It is true some general idea of this may be interpreted from the results obtained above, but the only conclusive information is to be gained by trying it.

In fact, some laboratories base their entire opinion of crude rubber upon the information gained by actual vulcanizing and physical tests which follow.

A certain test formula is agreed upon and all samples of rubber to be tested are milled up according to this and then subjected to vulcanization at a certain temperature. Samples are removed at equal intervals and thus the rate of cure in the rubber may be obtained. Tensile strength strips may then be made and the physical tests carried out. These are the tests which interest the practical man. Little does he care whether a sample of rubber runs high or low in resins if it will cure in a short time and produce what he regards as a good stock. The technical man, on the other hand, is interested in trying to figure out the relation and influence of each of the above tests upon the product finally to be obtained in actual working conditions.

In addition to all the foregoing information, before final judgment is pronounced in regard to a given sample of rubber, its life history should be known: where it came from, how it was obtained, to what species it belongs, how it was coagulated, how it was stored, its form, color, odor, and many more questions of a similar nature.

With all of this knowledge before one, a proper conclusion in regard to the merits of a sample of rubber should be easily arrived at.

Below is a table taken from Caspari, which shows the relations of different rubbers in regard to the three most important tests:

Rubber.	Washing Loss.	Resin.	Ash.
Para Hard Fine, Para, Bolivian Fine	16-21	2.5-3.5	0.2-0.4
Manaos Scrappy	20-25	1.6-2.0	0.6-0.7
Para Negrohead, Sernamby	30-40	3.0-6.0	0.5-1.5
Cameta	45-50	1.4-1.8	0.5-0.8
Mattogrosso Virgin	18-22	2.5-3.0	0.5-0.7
Mattogrosso Negrohead	20-25	1.5-2.0	1.5-2.0
Mollendo Fine	15-20	1.8-2.0	0.2-0.3
Mollendo Coarse	12-18	2.0-2.5	0.3-0.4
Caucho & Peruvian Ball	20-30	3.0-5.0	0.5-1.5
Manicoba	25-35	2.8-3.0	3.0-4.5
Ceara Negrohead	20-30	4.0-5.0	1.0-1.5
Mangabeira	30-40	20-25	1.0-1.5
Central American	20-40	4.0-7.0	1.0-2.5
Guayule	22-26	20-35	1.0-1.5
Sierra Leone, Conakry, Massai, Soudan	15-30	5.0-7.0	0.4-1.0
Bassam, Cape Coast, Accra, Labou, Ivory Coast, Gold Coast	25-40	7.0-11	0.7-1.0
Second-Accra Lump, Saltpond	30-40	29-38	1.4-2.0
Gambia, Bissao	30-50	5.0-6.0	1.0-2.0
Gaboon, Loango, Congo Ball	25-35	8.0-18	0.6-1.0
Lagos, Niger, Penin	30-40	10-25	0.3-0.7
Batanga, Cameroon	25-35	10-15	0.5-1.0
Lower Congo, Wamba	10-20	5-6	0.5-1.0
Angola, Loanda, Benguela	25-40	5-7	1.0-2.0
Upper Congo sorts	5-15	4-10	0.5-1.5
Mozambique, Beira	7-15	5-8	0.1-0.8
Madagascar, Tamatave, Majunga	20-30	7-10	0.2-0.5
Assam	15-35	5-11	0.5-1.0
Penang	15-30	5-7	0.3-0.7
Borneo	35-45	10-11	0.4-0.6
Java Plantation	1-2	5-6	0.3-0.4
Ceylon and Malayan Plantation	1-2	2.5-3.5	0.2-0.6
Plantation Rambong	1-2	7-8	0.2-0.3

CHAPTER XII

The Manufacture and Use of Inorganic Fillers

It will be our idea in this chapter to give the reader some information in regard to the manufacture of the materials which are used in compounding rubber and why certain materials are used. In the vast majority of cases, little is known of the substances used in compounding and it seems that the increasing of this knowledge should add interest to the subject and everyone will grant that increased interest tends toward greater efficiency.

Far be it from us to deal at any length with all the inorganic compounding ingredients, or even to mention them. We shall simply pick out what may be regarded as the commonest ones, those used in practically every factory to a greater or less extent.

In order to present this matter in some definite system, the writer will group these ingredients under four headings:

First—Substances essential for vulcanization.

Second—Accelerators.

Third—Fillers.

Fourth—Pigments, which will be subdivided into classes according to colors.

This is not the only classification and perhaps it is not the best one but it will serve our purpose here. These different groups overlap as will be seen from the order which follows.

Under the first group we shall consider sulphur, which we may say is essential in all processes of vulcanization; sulphur chloride; carbon bisulphide and carbon tetrachloride, which are used in certain kinds of vulcanization.

Under the second class, inorganic accelerators, the few we shall consider are the ones commonly used, namely:

Litharge,
White lead,
Sublimated white lead,
Red lead,
Lime,
Magnesia calcined,
Magnesia carbonate,
Magnesite.

Under the third class, fillers, we shall discuss substances which, as the name implies, may be obtained on the market at a price to enable the manufacturer to use them in large quantities, substances which chemically are more or less inert, such as

Barytes,
Alumina oxide,
Aluminum Flake,
Whiting,
Clays,
Silica (Atmoid),
Kaolin, China Clay.
Talc, Soapstone,
Fossil Flour,
Asbestos,
Blue Lead,
Magnesite.

There are several more which might be classified here but seem better to appear in the fourth group, pigments:

White Pigments

Zinc white,
Lithopone.
Zinc sulphide,
Barium sulphate.
Barytes,
Kaolin.

Red or Brown Pigments

Antimony Crimson,
Antimony Golden,
Rouge.
Red Ochre.
Vermilion.
Venetian Red,
Indian Red.

Black Pigments

Lamp Black,
Bone Black,
Hydrocarbon,
Graphite.
Lead sulphide.

Yellow Pigments

Yellow Ochre.
Chrome Yellow,
Cadmium sulphide.
Arsenic sulphide.

Green Pigments

Chrome Green.
Ultramarine Green,
Rinmann's Green.

Blue Pigments

Ultramarine Blue.
Thenard's Blue,
Prussian Blue,
Chrome Blue.

Above are the substances which will be dealt with in this chapter.

Sulphur

The substance, sulphur, with which every man in a rubber factory is acquainted, was also known to the ancients, for Homer 900 B.C. recorded that it was used in medicine and in fumigation. In 800, Gebir put forth the idea that all metals were compounds of sulphur and mercury and that it was possible to change from one metal to another by changing the ratio between these two substances. Lavoisier was the first to recognize it as an element.

The use of sulphur in rubber, however, remained a secret until Goodyear, in 1839, and Hancock independently in 1844, showed its effect upon rubber when heated in contact with it.

This element occurs in many different ways in nature and is well distributed over the earth. It is found in the free state in large quantities in Sicily and Louisiana. It occurs in the form of sulphides of the metals like iron, copper, lead and zinc; in the form of hydrogen sulphide in certain springs; as sulphur dioxide issuing from volcanoes; as sulphates of many elements like lead, barium, calcium, and strontium; then in organic substances like albumen, horn, etc. We must realize, therefore, the great distribution of this element in nature.

It has been estimated that the deposits of sulphur in Sicily, still untouched, contain fifty-five million tons, and that it will require about one hundred years to exhaust them. Up to the year 1900, it is claimed that 95 per cent of the world's production of sulphur came from Sicily, but in 1908, the United States produced 45 per cent of that amount, and from that date has continued to produce more and more.

Just a few words in regard to the methods used in Sicily and the United States for obtaining sulphur. In Sicily, the sulphur is found from 150 to 600 feet below the surface of the earth. It is reached by inclined winding shafts. In earlier times, all of the sulphur was brought to the surface upon the backs of men, women, and children, but modern methods of mining are in general use there now, and it is raised by mechanical means.

The ore is first graded into rich, good and ordinary lots. These ores were formerly made into piles and then fire was set to the piles. As part of the sulphur burned, its heat of combustion would melt the remainder, which would run down through the pile and collect in a trench around the original heap. This method, of course, caused a great loss, and in addition, the vapors of sulphur dioxide damaged the health of the people and killed the vegetation for miles around. By this method only about 25 per cent of the sulphur was actually obtained.

Next in line of advancement came the method of building larger heaps of ore and covering them over with earth, just leaving here and there shafts through the heap. Wood was placed in these shafts and kindled. Some of the sulphur would burn and thus melt the remainder, which was collected. These piles would require from one to two months to burn out. From these as high as 60 per cent of sulphur was obtained.

The next improvement came in 1880, when Gill proposed his regenerative furnace. He constructed two large brick chambers, which communicated with the same chimney so that while one was burning, the other might be in the process of charging. The combustion here could be more perfectly regulated, and as these chambers had a double bottom, thus separating the ore from the collected sulphur, a decided advance was made. As high as 75 per cent of the sulphur was obtained by this method.

The next great improvement came in 1891, when the removing of the sulphur from the ore was effected by the use of superheated steam. This was accomplished by building horizontal iron cylinders, equipped with a tight-fitting door and a track which would allow small iron cars, with perforated bottoms, containing the ore, to be run into this drum. The door is closed and steam at 130 deg. C. admitted, when the sulphur melts, runs to the bottom of the drum, which is slightly inclined, and then into a well which serves as a receptacle for the molten sulphur. This process is rapid, gives from 80 per cent to 90 per cent of the total sulphur, and does away with the objectionable sulphur dioxide fumes of the former methods.

All of these methods produce crude sulphur and this must then be refined. This refining process is accomplished by heating the crude sulphur in retorts and distilling it and condensing it in large chambers. If the temperature of these condensing chambers is above 114 deg. C., then liquid sulphur is obtained, which is drawn off into molds and known as brimstone. If the temperature is maintained below 100 deg. C., then flowers of sulphur will collect.

The deposits of sulphur in Louisiana occur about 1000 ft. below the surface of the ground. The method of obtaining this sulphur was suggested by Frasch. He drilled a well, similar to that used for extracting petroleum from the earth, then into this casing, he imposed three other concentric tubes, lined with aluminum, which would not be attacked by the sulphur. Superheated water was forced down through the outer pipe. When it came in contact with the sulphur, the latter melted, and was forced part way up the inner tube.

To bring it the remainder of the distance, aluminum pumps were tried but were not strong enough to support the strokes of the piston. The difficulty was then overcome by forcing air down the inner tube which emulsified the sulphur, thus making it very light and it rose to the surface. Here it was collected in large wooden boxes where it solidified.

By simply melting this sulphur again in iron boilers by use of steam and drawing it off into suitable molds, a sulphur of higher than 97 per cent is obtained. It is estimated that the Louisiana deposits contain at least forty million tons of sulphur.

Sulphur exists in three forms. The most stable is the rhombic variety which has a specific gravity 2.06 and melts at 114.5 deg. C. The monoclinic is next in stability and has a specific gravity of 1.92. Above 95 deg. C., the rhombic changes into monoclinic and vice versa. If boiling sulphur at a temperature of 445 deg. C. is poured into water, there results a form devoid of crystalline structure and called amorphous, or plastic sulphur. It resembles rubber in many of its physical properties but soon changes back into the rhombic variety. Therefore when sulphur is added to rubber and vulcanized at 45 lbs. pressure of steam that is equivalent to a temperature of 145 deg. C. and our sulphur must be above the temperature at which rhombic exists and in fact approaching the temperature at which the amorphous exists.

Rhombic sulphur exists in two modifications, roll sulphur or brimstone and flowers or flour of sulphur. It is the latter modification which is largely used in the rubber industry. In some places, they grind brimstone, sift it, and it gives equally as good results.

The flowers of sulphur results from the sublimation of sulphur as was pointed out above. Its specific gravity runs about 2.0 and it contains some modifications which are insoluble in carbon bisulphide.

It always contains some free sulphuric acid due to its slow oxidation. The sulphur should be examined from time to time to ascertain the amount of free acid, which should not show more than 0.2 per cent calculated as H_2SO_4. It should contain practically no ash, in fact the presence of any suggests adulteration, generally with an infusorial earth.

Sulphur is sometimes used in sulphur baths into which forms to be vulcanized are dipped, and here it serves simply as a heat carrier in the place of the more usual steam pressure or hot air.

Sulphur monochloride, S_2Cl_2, was found to have the property of combining with rubber to produce a substance resembling the sulphur vulcanized rubber. It has the power of entering into this chemical union at ordinary temperature, thus we have by its use what is known as the "cold cure" process.

It is made by passing dry chlorine gas over molten sulphur, when the two elements combine in the ratio of S_2Cl_2. It distills out of the apparatus and is condensed as a reddish yellow liquid with a boiling point of 138 deg. C and a specific gravity of 1.69. Moisture decomposes it in the following manner.

$$2\ S_2Cl_2 + 2\ HOH \rightarrow$$
$$SO_2 + 3\ S + 4\ HCl$$

Therefore when it is used in the rubber industry, moisture must be excluded as far as possible.

Sulphur is readily soluble in the monochloride and the monochloride is likewise converted into the dichloride by treating it with an excess of chlorine. So when examining the monochloride, we necessarily look for these two substances, sulphur and sulphur dichloride as impurities. The presence of these affects the boiling point of the monochloride and that gives us a very easy method of ascertaining the relative purity of our material. In commercial work, a range in boiling point from 130 deg. to 140 deg. C is allowed.

The dichloride has a boiling point of 64 deg. C, and it is a very objectionable impurity in any amount. The dissolved sulphur may run as high as 5 per cent. If more than this is present, the cured article will "bloom" or "sulphur up." This is determined by distilling off the chloride and extracting the residue with carbon disulphide, which dissolves the sulphur, placing the solution in a tarred flask, evaporating the solvent off and drying at 110 deg. C, when the sulphur remains and is determined.

Pure sulphur chloride should contain 52.5 per cent of chlorine. It is generally used for vulcanizing processes in a dilute solution of carbon bisulphide or carbon tetrachloride and the articles to be cured are dipped into this solution. The action is only a surface action and therefore may be used only with thin articles. In some cases the articles to be cured are subjected to the vapors of sulphur chloride when the desired reaction takes place and a glossy surface is produced. It finds extensive use in the manufacture of rubber substitutes. Its use here will be discussed at greater length in a chapter which follows and which deals entirely with the question of "substitutes."

Because of the use of carbon bisulphide and carbon tetrachloride in the "cold cure," it seems perhaps wise to devote a little space here in considering these substances.

Carbon bisulphide, like the chloride of sulphur, is made by the direct union of the elements. The apparatus for effecting this action consists of a tall, heavy walled cast-iron retort which is filled with carbon, generally coke, and heated to red heat. At the bottom of this retort, there enters a slow stream of molten sulphur which, coming into the retort, immediately changes into vapor and then combines with the carbon forming the bisulphide. This at the temperature of the retort is a gas and thus passes out the top into a system of condensers which first remove from the bisulphide any sulphur vapors which may have been carried along with it; then into a water condenser which condenses the bisulphide.

This is of course the crude product and for the majority of cases must be purified. This is done by adding to it a little lime water and shaking it, then placing it in a still with about a 1 per cent solution oil, a little water and some lead acetate. When the bisulphide is distilled out, it will represent a fairly good grade.

This substance is used very extensively outside the rubber industry. Up to 1850, however, practically its only use was in connection with the rubber industry, and then as to-day it was used as a diluent in the cold cure process, and as a solvent for rubber, hence coming its use in the preparation of rubber cements.

It boils at 46 deg. to 47 deg. C, and has a specific gravity of 1.27. It generally contains some dissolved sulphur, which may be determined by distilling 100 c.c. out of a tared flask. It should show at most two grams of distillation residue per liter. Having such a low boiling point, it evaporates very rapidly and with the air, forms a very inflammable mixture often causing bad fires. Its vapors are also poisonous and may produce serious results upon the workmen. The tetrachloride of carbon is made by passing dry chlorine through CS_2 in which contains a little iodine and a catalyst of asbestos impregnated with magnesium chloride is suspended. The reaction takes place as follows:

$$CS_2 + 3\,Cl_2 \rightarrow CCl_4 + S_2\,Cl_2$$

These two products may be separated by distillation, but it has been found that in the presence of a little powdered iron, the following reaction will take place:

$$CS_2 + 2\,S_2\,Cl_2 \rightarrow CCl_4 + 6\,S$$

These resulting products are separated by distillation and the sulphur is used to produce carbon bisulphide again.

The tetrachloride is purified by washing with a solution of caustic soda and then distilling from a solution of calcium hypochlorite. It boils at 77 deg. C. and has a specific gravity of 1.63. It is an excellent solvent for fats and resins and has the great advantage of not being inflammable. It even has the power of rendering certain inflammable solvents uninflammable when it is added to them. Its great use in the rubber industry is that it is mixed with coal tar naphtha and will produce non-inflammable rubber solutions, and likewise its use as a diluent in the cold cure process.

To test the commercial variety of the tetrachloride, it should distill between 75 deg. and 78 deg. C. and leave no residue. The determination of its specific gravity will generally reveal the presence of any adulterants.

Inorganic Accelerators

The second group of materials we called inorganic accelerators or " sulphur carriers " as they have sometimes been called. The theories advanced in explanation of their action in hastening vulcanization will be reserved for the chapter dealing with the theories of vulcanization.

The one which has been used to greatest extent is probably litharge, the monoxide of lead. It is made by heating the metal lead in a reverberatory furnace with a current of air passing over it. It requires some time for the oxidation to be complete and must also be watched that some of the other oxides of lead are not formed. The yellow powder formed in the above process is called Massicot. When this is melted and then allowed to cool rapidly, the mass which results is called litharge. It has a specific gravity of from 9.2 to 9.5. Considerable litharge is also made to-day in connection with the refining of silver. The lead is removed from the molten silver when it is oxidized with a current of air to the monoxide. It then floats on the surface of the silver and is removed.

Litharge is generally supplied in a high state of chemical purity, but varies considerably in degree of fineness and this of course has an influence upon its color. Litharge is slightly basic and therefore tends to absorb carbon dioxide, which is objectionable. A sample should therefore dissolve in dilute nitric acid without any effervescence, and without leaving a residue of the dark colored lead peroxide, which is very objectionable.

It may contain some unoxidized metal, which does no harm and may be detected by dissolving the litharge in acetic acid instead of nitric. It is always well to test the resulting solution for copper as that is objectionable even in small amounts.

Litharge might well be classed under the heading of Black Pigments as it imparts that color to the vulcanized rubber due to the formation of its sulphide. Until recently, nearly all of the black and dark gray rubbers were colored with litharge but at present it is used largely on account of its accelerating action upon vulcanization.

White lead is a basic carbonate of lead and has an accelerating action upon the rate of cure but to a less degree than litharge. As a pigment, it does not possess the coloring power which litharge has. It gives the article more of a bluish gray color.

It is made by several different methods, some requiring a long period of time, others proceeding more rapidly. From the white lead manufacturer's point of view, the rapid method is naturally the one to be preferred, but from the consumer's viewpoint, the products of the slow process seem to be desired most.

The Old Dutch Process consists in subjecting lead plates to the action of acetic acid and carbon dioxide formed by fermentation. This first produces the acetate of lead, then the basic acetate, and finally after a lapse of five or six weeks, the basic carbonate, a white lead, results. The white lead is freed from any unaffected lead or acetate by washing with water. The Germans have a quicker method where they blow steam and acetic acid vapors into chambers containing lead plates and then bring into these same chambers carbon dioxide from a coke furnace and the basic carbonate of lead results. It is washed and dried, and ready for market.

The French dissolve litharge in acetic acid forming the basic acetate and then pass carbon dioxide through this until the white lead formed, which settles to the bottom, is transferred to a filter press, dried and ground.

The Russian white lead is made by producing the neutral lead carbonate by the action of carbon dioxide upon the basic acetate of lead. The neutral carbonate is then made into a paste with water, about 1 per cent of lead acetate added, and also 30 per cent of lead oxide. The whole mass is stirred in the cold with the addition of a little water until it all hardens. In from three to four hours, the process is complete and a fine grade of white lead results.

There is a method whereby the freshly precipitated lead sulphate is converted into the basic sulphate by heating with caustic soda, then when this solution is heated with sodium carbonate, the white lead is precipitated. In this country, atomized lead is produced by blowing a jet of steam against small holes where molten lead is issuing. This "lead sand" is then treated with dilute acetic acid for about seven days, while air, carbon dioxide, and a little steam are blowing through the vats. White lead results which is washed from the unaltered lead.

The water of hydration which may be present in white lead often causes "blowing." It has a specific gravity of 6.1 to 6.2.

Sublimed white lead is not what the name implies, a carbonate of lead, but is a basic sulphate. Its use is increasing in favor as it does not tend to produce "blowing." It accelerates more than white lead, and produces a black product when vulcanized. It is a velvety powder and mixes readily with the rubber. It has a slightly higher density than white lead.

Red lead, or minium, is the tetroxide of lead, or really it may be thought of as a mixture of lead monoxide and dioxide.

$2\ PbO + PbO_2 \rightarrow Pb_3O_4$ (Red Lead)

It is made by heating litharge in a reverberatory furnace at a temperature of 450 deg. C., but must not be allowed to melt. The best grade is made by heating the monoxide of lead with sodium nitrate in an oxidizing flame to a dark red heat. It has a specific gravity of 8.6 to 9. It is one of the most powerful inorganic accelerators, perhaps due to the heat of reaction between it and the sulphur. It is used in rapid curing stocks. It can be used only within certain limits as it will attack the rubber as a result of its strong oxidizing power.

The adulterants that must be looked for are calcium carbonate, barytes and ferric oxide.

Under the term "Lime," we largely, in connection with rubber, refer to the hydroxide of calcium which is "slaked lime," in contrast to "quick" or "burnt lime" which is the oxide of calcium. The latter is made by heating limestone, which is calcium carbonate, in kilns to a temperature of 1,000 deg. when it loses its carbon dioxide and quick lime results. When this is mixed with about one-third of its weight of water, the white, powdery, swollen mass of slaked lime results. If more water is added, the soluble alkalies are washed out and a softer powder will result. It has a specific gravity of 2.1 and has a finer grain than the quick lime. It is added only in small proportions.

In small quantities, it takes up the moisture which may be present in a stock and thus prevents blowing. It has the power of combining with the free sulphur and thus tends to prevent "blooming." Excess of lime tends to diminish the resiliency of rubber and also makes it harder, having that effect even in hard rubber articles. It also has an accelerating action upon the rate of cure.

Lime should be fairly free from carbonate and silica and upon ignition show close limits to that of $Ca(OH)_2$, that is, 24.3 per cent. Manganese is sometimes present in lime and renders it useless for the rubber manufacturer. It affects rubber in the same manner as copper does.

There are several forms of magnesium compounds in use. We have two kinds of calcined magnesia (which is the oxide), known as "heavy" and "light" calcined.

If to a hot solution of a magnesium salt, a hot solution of soda is added, there will be formed what is known as heavy magnesium carbonate and when this is calcined, the heavy magnesia results. If, on the contrary, cold solutions are used, the light carbonate will be formed, and when this is calcined the light magnesia results. The only difference therefore is in the structure of the two.

It is used in the same manner as lime. Its specific gravity is 3.2 to 3.6 and it is a little coarser grained. It possesses marked accelerating power upon the rate of cure and also increases the toughness of the product more than 10 per cent except in rapidly curing stocks.

The magnesias suffer varying ignition losses ranging from 2 to 20 per cent. When a compound has been made up with a certain grade of magnesia, then deliveries which follow should not be allowed to vary much from the ignition loss of the original. Rubbers running high in resins seem to give better results when compounded with magnesia.

There occurs in nature the mineral, magnesite, which is the carbonate of magnesium, of sufficient purity that it may be used in compounding. The carbonate is also artificially made as pointed out above.

These substances possess very little accelerating power, and are used largely as fillers. As fillers they may be employed up to 30 per cent without seriously injuring the rubber.

Under the third division of our subject, fillers will be considered in the meaning which the word itself implies: substances which are not used on account of any good property which they impart to the rubber, nor on account of any color which they may produce in the finished product. In other words, they are cheap materials which to a certain extent may be used in the place of more expensive substances. Their amount is regulated by experiment so that too much will not be used and thus impair the finished product.

Barytes

The first one of these for consideration will be barytes, or heavy spar. It is found in nature in a comparatively pure form, in fact, in so high a degree of purity that it needs no other preparation than that of grinding to a fine powder. It may be found in shades varying from a good white to a gray, depending upon the per cent of barium sulphate present.

It is obtained also by artificial means. First, the mineral or natural sulphate is heated in a furnace with carbon when there results the sulphide and oxide of barium. These are then dissolved in water and sodium sulphate added and the insoluble artificial barium sulphate, barytes, is precipitated.

Second. it is made by dissolving

the mineral crite, which is the carbonate of barium, in hydrochloric acid, and then adding sodium sulphate, when the barium sulphate results.

It has a specific gravity of 4.5 to 4.6 and is obtained very often under the name of " permanent white " or " blanc fixe." Due to its high specific gravity, it is employed to increase the specific gravity of some stocks. The artificial product is to be preferred to the natural one as it is amorphous while the ground mineral, even though it is reduced to a fine powder, still retains more or less its crystalline structure. It is used to adulterate white lead, and to a certain extent, has the advantage of not being effected by hydrogen sulphide or metallic sulphides.

Aluminum Compounds

There are several compounds of aluminum which are used as inert fillers.

" Aluminum flake " is a natural product coming in several different colors from white to gray and gray to brown. It has a specific gravity of 2.5 to 2.6 and is used to a certain extent in place of zinc oxide.

Aluminum oxide does occur in nature but the artificial product is the one desired for use in rubber. In the Bayer process the mineral bauxite is calcined and pulverized, mixed with a little lime and then treated with sodium hydroxide solution of 45 de. Bé, at a pressure of three to four atmospheres. Sodium aluminate results which is soluble in water. It is then filtered hot and, after suitable dilution, pure gelatinous aluminum hydroxide is added. It is then agitated for from five to six days when all of the aluminum is precipitated both from the bauxite solution and from that which was added. It is then recovered by a filter press, and thoroughly dried, when a fine white powder results with a specific gravity of about 3.9. It was with the use of this oxide that Eaton suggested the making of a pure white rubber.

The hydroxide of alumina is now coming into use in some factories. It is one of the lightest gravity materials possible to obtain.

Kaolin, or China clay, is a natural occurring product. In chemical composition it is a hydrated silicate of alumina. It acts as an inert filler in all the rubber compounds. It has a specific gravity of 2.3 to 2.6. It should show an ignition loss of 11 to 14 per cent and should not be attacked by dilute acids. It often runs very high in moisture which, of course, must be guarded against.

Talc

Talc is a silicate of magnesia occurring native in the earth in a sufficiently high state of purity so that it may be reduced to a powder and used directly in the industries. It is not used to any great extent in rubber stocks but is employed a great deal in all kinds of work to prevent surfaces from sticking together. Molds are dusted over with it to keep the rubber from adhering to them during vulcanization. Some goods are buried in it during vulcanization.

Talc has a specific gravity of 2.7. When it is used in compounding, it imparts to the rubber, smoothness and stiffness, and also increases electrical insulation when used in cable coverings. A common adulterant is calcium carbonate, which is detected by the effervescence when treated with an acid.

Soapstone is really a form of talc and as such, is used in large quantities.

Silicon Oxides

There are other materials on the market under different names which are in reality the same from a chemical point of view. Silica, Atmoid, Infusorial Earth, Fossil Flour and Mountain Flour are all names given to the oxide of silicon. This material occurs in a great many different forms in nature. All forms are without material effect upon rubber compounds, other than stiffening the product to some extent. They have a low specific gravity ranging between 2.7 and 2.9.

These materials consist of the skeletons of microscopic animals. Large deposits are found in Nova Scotia and Germany.

Asbestos

Asbestos is a silicate of magnesia with a varying amount of the magnesia replaced by lime, together with ferrous oxide and alumina. Large deposits of it are found in Italy, Canada and Cape of Good Hope. It is used both as fiber and as powder. The fibrous form is used in mechanical goods for it increases the toughness and unyielding quality of the structure. It is used in goods that are subjected to a high temperature and also in articles like brake blocks.

Calcium Carbonates

Chalk or whiting is the carbonate of calcium. It occurs in nature in several modifications, as limestone, chalk, and marble. The chalk deposits are the remains of microscopic marine animals. Chalk is obtained in a fine white grade.

Whiting is really purified chalk, made by grinding the chalk, then floating it and the fine white sediment is obtained by running it through a filter press. It is then dried rapidly. If, during the drying, too high a temperature is used, the product will feel harsh. As it is slightly deliquescent it must be kept in a dry place; otherwise it may cause trouble in the stock where it is used.

Large quantities of whiting are used in the rubber business on account of its cheapness. It has a specific gravity of 2.7 to 2.9. It will increase the resiliency of rubber and also increase its hardness without producing the " stony " effect that other ingredients do.

Sulphides

We find in nature mineral deposits of the two sulphides of lead and zinc. If such ore is smelted with a mixture of coal and lime, it produces what is known as Blue Lead. It is an extremely fine powder and possesses a high specific gravity. It is a cheap product and, to a certain degree, hastens the rate of cure in the stocks where it is used. Therefore, it may be used in the place of litharge and will also produce the fine black product.

Magnesium Carbonate

Magnesium carbonate, which was mentioned under the first class, is also used as a filler.

White Pigment

Under our third group, White Pigments, may be discussed materials which might have been grouped under fillers. This will be true of all the divisions which follow.

Zinc Oxide

The first and most important of the white pigments is zinc oxide. No one pigment is used as extensively as this one in the manufacture of white rubber goods.

It may be made by roasting any one of the zinc ores, but the best method is that of burning the pure metal. The trouble with roasting the ores lies in the fact that lead, iron, and copper are very often present in these and thus will be found in the finished product.

A good sample of zinc oxide should dissolve completely without effervescing in a 10 per cent solution of acetic acid. If it is desired to test for the presence of iron, lead or copper, in the oxide, all that is necessary to do is to dissolve the specimen in dilute hydrochloric acid, and conduct hydrogen sulphide into it. If it is free from the above metals, there will be no preciptate formed.

Inferior grades of zinc are often adulterated with barytes, whiting, or kaolin and the presence of these will be detected when the sample is treated with acetic acid. The barytes and kaolin are both insoluble and the whiting will produce the effervescence. White lead is sometimes an adulterant.

Zinc oxide has a specific gravity of 5.5 to 5.6. Although it is one of the extensively used white pigments, yet it is not all that is to be desired. Its covering power is only moderate and during vulcanization, it turns to a yellow color. The higher the temperature and longer the period of vulcanization, the more pronounced this color becomes.

Another defect of zinc oxide is the fact that dilute acids will dissolve it out of the vulcanized rubber goods. As a result of this, certain countries prohibit its use in rubber articles which come in contact with foods or beverages in their preparation.

Zinc Sulphide

A white pigment which has increased in favor rapidly is zinc sulphide. It occurs in nature in the mineral known as zinc blende, but the product used in rubber is an artificial one. It may be produced by causing zinc dust and vapors of sulphur to come together at an elevated temperature. It may also be produced by precipitating it from a solution of zinc with ammonium sulphide.

It is a white powder with a specific gravity of 3.3 and possesses greater covering power than the oxide. It has the distinct advantage of not changing to the yellow tint during vulcanization, and it is not leached out of the rubber by dilute acids as is the oxide. It is liable to the same adulterations as the oxide is plus the oxide itself. The best grades of zinc sulphide should run as high as 90 per cent. purity.

A very good method of determining its purity is to place about 0.2 of a gram of the dried material in a flask and shake it up with 50 c.c. of N/10 iodine solution. Five c.c. of concentrated hydrochloric acid are then added and the whole is allowed to stand a couple of hours with occasional shaking. By this time, all of the white particles should have disappeared and the excess iodine is then titrated with sodium thiosulphate solution. Each c.c. of the iodine solution which reacted with the hydrogen sulphide, produced when the acid was added to the zinc sulphide, is equivalent to 0.00485 grams of the sulphide. Thus its purity is easily calculated.

Lithopone

Another zinc pigment which was first used in paint and now extensively in rubber, is one known as lithopone. It is an artificial product, made by bringing together solutions of barium sulphide and zinc sulphate, when the following reaction takes place:

$$\mathrm{Ba\,S} + \mathrm{Zn\,SO_4} \rightarrow \mathrm{Ba\,SO_4} + \mathrm{ZnS}\downarrow$$

The resulting product is insoluble and is a compound of zinc sulphide and barium sulphate which is known as lithopone. It has a specific gravity of 3.8 to 4.2 and should contain 70.5 per cent of barium sulphate and 29.5 per cent of zinc sulphide. It varies considerably, however, from these per cents, depending upon the method of preparation.

Of course, the valuable part of it is due to the zinc sulphide and there is a standard grade of lithopone, known as "Blue Seal," which is guaranteed to have 30 per cent of zinc sulphide. For general purposes it is necessary only to examine a sample for moisture, acid insoluble, and sulphide.

The acid insoluble is determined by boiling one gram of the dried sample with concentrated hydrochloric acid, diluting and boiling again and then filtering, drying and igniting the residue in a platinum crucible, and then weighing. This residue should not exceed 70 per cent.

To detect the presence of kaolin as an adulterant, a little hydrofluoric acid may be added to the residue, evaporated off, and reweighed, and any loss in weight represents the presence of silicates.

What was said in regard to the use of zinc sulphide may be said of lithopone.

Barytes and Kaolin

In addition to these white pigments, may be mentioned barytes and kaolin, which were considered under fillers.

Red Pigments

The next class of pigments for our consideration are those which impart a red color to rubber goods.

Golden and Crimson Antimony

The first to be mentioned are Antimony Golden and Crimson, and these two are divided into grades according to color, for instance, Golden No. 1, Golden No. 2.

The Crimson Antimony is little used by itself but is made by boiling together antimony trichloride and thiosulphate solutions, when the trisulphide of antimony is precipitated.

Colors varying from this crimson to orange are then produced. the shade depending upon the conditions of precipitation or upon the respective percentages of crimson and golden sulphides in the mixtures.

The golden sulphides are the ones in commonest use. These are made by boiling powdered stribnite, which is the mineral containing the natural sulphide of antimony, with alkaline polysulphides when there results sulfantimonate in solution. When this sulfantimonate is treated with hydrochloric acid there will be precipitated a mixture of the sulphides of antimony and also some free sulphur resulting from the polysulphides.

One form of the orange antimony is co-precipitated with hydrated calcium sulphate and is called "plastered antimony." This grade, of course, is cheaper and does not contain as high a percentage of the red pigment.

When it comes to determining the true worth of a sample of antimony, the best method is to subject it to actual vulcanization experiments, because it is found that some antimonies will not hold their color during vulcanization. This fact cannot be ascertained by chemical tests.

In analysis the following determinations are generally made: moisture, free sulphur, antimony, calcium sulphate, sulphide-sulphur.

The free sulphur present is what led many to believe for a long time that antimony red was a vulcanizing agent. In fact, even now some manufacturers claim that they obtain better results if they mix the sulphur into the antimony which they use in the compound. To supply such a demand the producers of sulphureted antimony put free sulphur into it up to the extent in certain cases of 40 per cent. It is determined by extracting a weighed amount of antimony in a Soxhlet extractor with carbon disulphide or acetone for about eight hours. The solvent is evaporated and the amount of free sulphur calculated.

The antimony itself, iron and calcium sulphate are determined in the usual manner. The sulphide sulphur is calculated by determining the total sulphur in the extracted sample and subtracting from this the sulphur present in the sulphate.

In connection with the use of the sulphides of antimony, we shall publish some of its merits as put forth by a prominent manufacturer:

"*First*—Antimony Sulphuret used in the curing of rubber acts as a sulphur carrier causing all of its free sulphur to unite with the rubber. Sulphur added as a sulphuret is taken up completely by the rubber. Therefore it is not necessary to add an excess of sulphur.

"*Second*—On account of the above, 'blooming' does not take place for practically none of the sulphur is left uncombined in the rubber.

"*Third*—On account of the above, vulcanization can be carried on at a lower temperature; thus the tendency to overcure is diminished.

"*Fourth*—On account of the above, the rubber has a longer life. It can be kept much longer than gray rubber before it will begin to deteriorate.

"*Fifth*—It has more elasticity. This is shown by the following test: A piece of red rubber tubing and a piece of gray tubing are bent firmly and pressed with a spring clothespin clip. The two samples are allowed to stand in the sunlight for several days when the clips are removed. It will be noted that the properly antimony-cured red tube will spring back into its original shape immediately upon removal of the clamp. The gray tube goes back into its old form slowly. In use this is noticed when a tire goes flat over night. The red tube allowed to bend by the weight of the car will immediately spring back into place when the weight is removed. The gray tube will remain bent even after the weight of the car is lifted.

"In a large lot of returned shelf goods, half gray and half red, the following was noticed. The gray tubes when removed from the cartons were in bad shape. They could not very well be unfolded as their creases seemed to be permanent. The red ones, however, were in just as good shape as the day when they left the plant more than a year before and they were simply transferred to new cartons and placed on sale. The gray tubes were covered over with a thick coating of sulphur bloom while the red ones were entirely free from bloom. The superintendent of the plant pointed out the fact that the only difference between the two stocks was that the gray ones had obtained all of their sulphur from sulphur flour while the red ones obtained the larger part of their sulphur from antimony sulphuret."

Due to the oxidization of the sulphur, we find that most samples contain free sulphuric acid. The amount should never exceed 0.06 per cent.

Iron Sesquioxide

There are several terms used for practically the same ingredient, the sesquioxide of iron. We see it sold as rouge, red ochre, venetian red, red hematite and under a few other names. In general use they are all inferior to the antimony colors, but they are useful in the manufacture of non-poisonous articles and hard rubber, where it behaves better than the antimony.

Rouge

Rouge is made by calcining the sulphate of iron and if this is done in the presence of barium or calcium sulphates, a more brilliant color is obtained. It has a specific gravity of 5.0 to 5.2.

Red Ochre

Red ochre is made by heating yellow ochre, which is a clay containing siliceous matter along with a hydrated iron oxide. So the red ochre is really a rouge diluted with a siliceous matter and is consequently of less value than the rouge.

Red Hematite

Red hemitate is the mineral ferric oxide and is of sufficient purity and of such a color that it is used as a red pigment in ebonite and articles that must be heat-resisting.

Venetian red and indian red are artificial ferric oxide.

Vermilion

Vermilion is a sulphide of mercury and is the most brilliant of all red pigments, likewise the most expensive, therefore, not used so extensively. It is employed in dental rubbers and must be free from all soluble mercury salts.

It occurs in nature as the mineral cinnabar. It is produced artificially by heating the black sulphide in a covered cast-iron pot and the cinnabar will be sublimed. This is often purified still further.

It is adulterated with iron oxide, red lead and sometimes gypsum. Its purity is easily tested by heating some in a porcelain dish. If no adulterant is present it will completely volatilize, leaving no residue.

Black Pigments

Under black pigments occur largely different grades of carbon, the commonest being lampblack.

Lampblack

This is made by collecting the carbon which results from the incomplete combustion of oils, fats, resins, coal and like organic bodies. As a result of the varied starting out materials, we naturally get varying grades of lampblack. It generally contains some greasy materials and the amount of these present should be determined by an acetone extraction.

Lampblack should not show more than 5 per cent of grease and should leave practically no ash. Lampblack has a specific gravity of 1.8 and has come into extensive use just recently.

A short time ago it was used only in boots, shoes, carriage cloth, and druggist supplies but today it is one of the important ingredients used in a large number of mechanical goods and extensively in tire stock, where it appreciably increases the strength of the stock as well as its wearing surface.

Bone Black

Bone black is obtained by calcining defatted bones in closed vessels out of contact with air. This grade of carbon, therefore, runs very high in mineral matter, very often equaling 90 per cent of the whole. It is coarse and harsh, even after grinding, and, although a black pigment, finds only limited use.

Gas Carbon

Gas carbon is a pure grade of lampblack which is quite popular with certain manufacturers at present.

Black Hypo

Black hypo is a pigment which has been used in the past to some extent but is received with less favor at present. It is made by heating together a mixture of litharge, sulphur and lampblack. The composition of the resulting product is uncertain. It contains some lead sulphide, a little free sulphur and some of the lead salts of oxygen sulphur acids. It has been made by adding sodium thiosulphate to a solution of sugar of lead, when lead thiosulphate is precipitated, and is sold as white hypo. If, however, this is heated, it changes to black, due to the formation of the sulphide. During the vulcanization process, if white hypo has been used, it will suffer the same change and produce a black rubber. Its use at present is waning.

Graphite

Graphite is a form of carbon occurring in the free state in a high degree of purity and is also an artificial product today. It is made in electrical furnaces, where coal is subjected to a very high temperature for a period of twenty-four hours.

Graphite is used in rubber goods more as a filler perhaps than as a pigment. Its coloring power is not very great. It will stiffen rubber articles and has remarkable lubricating properties, preventing the rubber from sticking to metals. It is used in the compounding of steam jointings and goods that are going to be subjected to a high temperature.

Lead Sulphide

Lead sulphide is also used as a black pigment, whether it is added as such or in the form of some other lead salt which changes into the sulphide during vulcanization. It is the most abundant form of lead found in nature as galena.

Yellow Pigments

Now we will mention some of the common yellow pigments.

Yellow Ochre

Just as we had a red ochre so there is a yellow ochre. The red variety is the pure ferric oxide, but if this is mixed with clay or siliceous matter, it loses its red color and varying shades of orange and yellow result. It is a natural occurring product and is inert in rubber. It is very cheap and the color it produces in rubber lacks brilliancy.

Chrome Yellow

Chrome yellow is the chromate of lead and is made by adding a solution of sodium chromate to a solution of lead acetate, when the yellow precipitate is produced. It finds extensive use in the manufacture of toys and cold cured goods, where its lead content does not interfere.

Cadmium Yellow

Cadmium yellow, which is the sulphide of the metal, is one of the best yellow pigments. It is made by passing hydrogen sulphide into a solution of a soluble cadmium salt. It gives to rubber a fine yellow color and is not affected by vulcanization. It may be used in toys as it is non-poisonous. The cost of this material has practically eliminated its use.

Arsenic Trisulphide

Arsenic trisulphide is an excellent yellow pigment as it is not affected by vulcanization, but it is so extremely poisonous that its use has been almost abandoned. When it is mixed with a small amount of zinc oxide, it will produce a beautiful cream colored yellow.

Yellow Dyestuffs Used

The yellow colors are found largely, however, in toys, surgicals and tilings, and beside the pigments mentioned above, to-day we find large quantities of organic dyestuffs being used instead of the mineral pigments.

Green and Blue Pigments

Green and blue pigments are used in the same line of goods as the yellow ones, and they too are being replaced by the organic dyestuffs. A few of each, however, are still important enough to be mentioned.

Chrome Green

Chrome green is the sesquioxide of chromium. It is made by melting together one part of potassium dichromate and three parts of boric acid, then dissolving out the potassium borate, when there will remain the beautiful green powder. It is inert in rubber and is not affected by vulcanization.

Rinmann's Green

Rinmann's green is made in almost any shade of green desired. Chemically it is zinc cobalt oxide and by varying the two metals, different shades are produced. It is made by calcining the precipitate formed when a solution of sodium carbonate is added to a solution containing the sulphates of zinc and cobalt. It gives a fairly good green color in cold cured goods.

Ultramarines

On the border line between the green and blue pigments, we find the very interesting substance known as ultramarine, existing as a green pigment or a blue one depending on its method of preparation.

No one knows to what it owes its color. It is made by heating to bright redness in a covered crucible for three or four hours an intimate mixture of 100 parts of pure kaolin, 100 of dried sodium carbonate, 60 of sulphur and 12 of charcoal. Chemically we should expect such a mixture to give the silicate of sodium, the aluminate of sodium, and sodium sulphide, which might give the whole mixture a brown color, but on the contrary the mass is green and is known as ultramarine green. It is a permanent color and is used as an inert pigment.

If this green is powdered, washed with water and dried, then mixed with one-fifth of its weight of sulphur and gently roasted until the sulphur is removed, and this repeated again perhaps if necessary, the residue will possess a beautiful blue color and as such is known as ultramarine blue. This is used in the production of blue rubber articles, tiling, etc.

Acids have the power of destroying both the green and the blue color of these ultramarines.

Prussian Blue

Prussian blue is made by adding a solution of potassium ferrocyanide to a solution of a ferric salt. The blue pigment formed is filtered, washed and dried. This blue compound will produce a blue stock but not quite as good as ultramarine. It may be used when an acid resistant material is needed and ultramarine cannot be used. On the other hand, however, alkalis will decompose it. Prussian blue does not withstand the effect of vulcanization as well as ultramarine blue.

Thenard's Blue

Thenard's Blue is made by heating together in a covered crucible aluminum and cobalt phosphates. The blue color which is obtained will depend upon the proportion of aluminum and cobalt used: the more cobalt employed the darker will be the shade of blue. This pigment is not used to any great extent.

In these two chapters, which, on account of the material they contain appear very choppy, we have tried to give the reader a little insight into the commonest of ingredients used in the rubber industry.

CHAPTER XIII

The Manufacture and Use of Organic Accelerators

In the minds of some people there seems to exist a misunderstanding in regard to the terms " accelerators " and " catalysts." Therefore it does not seem out of place here to point out the true meaning and correct use of the two terms.

Brezelius knew that hydrogen peroxide, if allowed to stand by itself, decomposed very slowly into water and oxygen. He also knew, however, that if to this hydrogen peroxide was added a small amount of finely divided platinum, a rapid decomposition of the peroxide took place and a great volume of oxygen was liberated.

He went further and found out that the platinum was not changed in itself in any way and that a small amount of platinum was capable of transforming an indefinite amount of hydrogen peroxide into water and oxygen. The two elements, hydrogen and oxygen, will remain mixed together at ordinary temperature almost indefinitely without any chemical union, but if a little platinum sponge is introduced into the mixture, the union immediately takes place, yet the platinum remains unchanged.

Sulphur dioxide does not combine with oxygen under ordinary conditions but in the presence of platinized asbestos, the two react and form the anhydride of sulphuric acid, thus the production of sulphuric acid today by the " Contact Process."

By these three examples it will be seen that certain reactions are made to take place under certain conditions, by the addition of what might be regarded as a foreign substance. This foreign substance is necessary to change the speed of the reaction and is not changed in the least by it as far as we know. Such substances Brezelius called " catalysts," their action he called " catalytic " and the phenomenon " catalysis." Catalysts will not incite reactions to take place which would not take place at all but they do wonderfully affect the speed of these reactions.

Action of Catalysts

It has been suggested that these catalysts, in effecting their work, form intermediate products which are very unstable and break down giving the products of the reaction and the renewed catalyst. Such intermediate products have been proved to exist and to these has been given the name " pseudo-catalytic phenomena." Ostwald however proposes the idea that they act like a lubricating oil in a rotating wheel. It turns very slowly and with great difficulty when oil is lacking but when it is added, the wheel turns freely yet the oil has no part in the movement. Here will be seen the analogy to catalytic action.

Euler has advanced the hypothesis that the velocity of a reaction depends upon the free ion concentration and that catalysts have the power of modifying this concentration, for we have, beside these catalysts which increase the speed of a reaction and are called " positive catalysts," those which retard a chemical change and are called " negative catalysts." Here we have set forth the true conception of catalizers, namely substances which may hasten or retard a chemical change and yet are not themselves affected in any way.

The term accelerators has quite a different meaning and application from a chemical point of view. In the first place, they only increase the velocity of the chemical changes and secondly they may or may not be affected chemically themselves.

In the rubber industry, therefore, we should refer only to accelerators, for in the vast majority of cases, the substance which is added to increase the speed of vulcanization is in itself changed also.

Accelerators

Only recently did it occur to the rubber chemists that it was possible to cut down the length of time of vulcanization, without increasing the steam pressure, by introducing into the rubber very small amounts of organic substances which would act as accelerators. Once tried and the results observed, the commercial importance of the practice was immediately grasped.

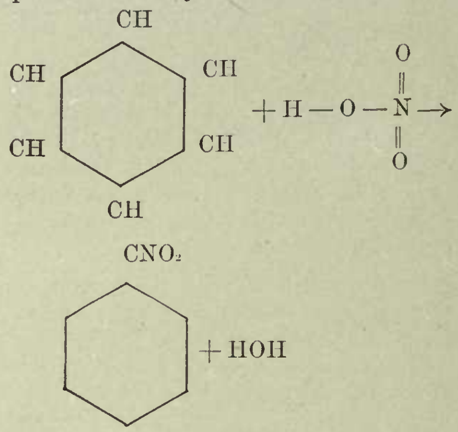
The introduction of these substances was suggested from the fact that synthetic rubber, or caoutchouc was very difficult to vulcanize, as is also acetone extracted rubber. This led to the study of ways to vulcanize the synthetic product and to the study of the acetone extract from Para with the result that nitrogenous bodies were found in the extract and the introduction of these into caoutchouc shortened its time of vulcanization.

The work of research laboratories was directed toward the producing and perfecting of substances and learning also how they might be used. It is in the midst of this kind of work that we find ourselves today. In fact we do not know very much about this new line as yet and we must still be very modest in our claims. Many organic substances have been experimented with in this connection and new ones are being recommended and placed on the market every day. Some of them appear under their true chemical title while others are disguised under trade names. Recently this laboratory received one from a commercial house with the request that some experimental work be done with it and with the statement that they had not named it as yet.

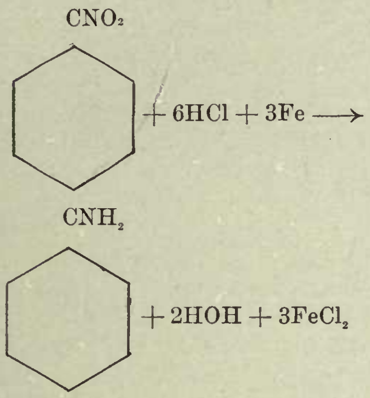
Several theories have been advanced as to the part which these substances really play in hastening the cure of rubber articles, but we shall leave those to a future chapter.

In this section we shall consider only a few accelerators and those are the ones in commonest use. It is held today that only nitrogen compounds will act as accelerators, and only those capable of being easily handled, easily incorporated into the stock, and possessing great enough stability not to produce "blowing" during vulcanization, may be used. One of the first substances of this kind to be used was aniline.

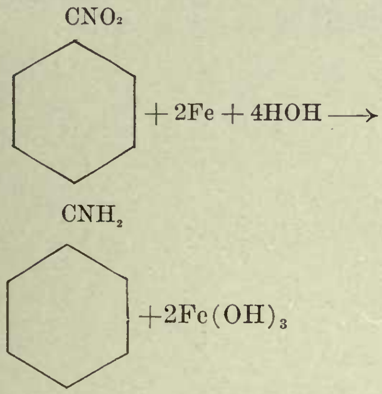
Aniline is made from nitro-benzene, which is made from benzene. This is effected in large cast iron vessels where a mixture of nitric and sulphuric acids is gradually poured into benzene. It is constantly stirred and the temperature maintained at 25 deg. During the latter part of the reaction the temperature is raised to from 70 deg. to 90 deg. The mixture is then forced into a conical tank when the acid mixture settles to the bottom and is drawn off. The nitrobenzene is washed several times with water and then distilled in a current of steam. The equation for its production may be indicated thus.



The nitrobenzene is then placed in a cast iron cylinder provided with a stirrer, a reflex condenser and an opening for introducing iron filings. Some water is placed in the cylinder, some iron turnings and hydrochloric acid. These are kept stirred while nitrobenzene is added. The reaction may be started by a jet of steam. Afterward, however, it will maintain its own temperature for operation, in fact one must guard against its getting too hot. At the end of the operation we have aniline, aniline hydrochloride, ferric oxide, some unaltered nitrobenzene and other impurities. The main reaction which has taken place may be represented thus.



But in actual working conditions it requires only about one-fourth of the theoretical amount of hydrochloric acid, thus showing that after a certain concentration is reached, the reduction is then effected by the action of iron on water in the presence of ferrous chloride in the following manner:

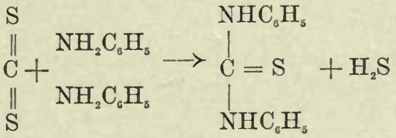


After the reduction is complete, thick milk of lime is added until a distinct alkaline reaction is obtained when the mass is distilled with steam. The distillate will separate into two layers, the aniline being in the lower portion. This is often purified by redistillation. Aniline has a boiling point of 183 deg. to 184 deg. and a specific gravity of 1.024 at 16 deg. C. It is colorless when pure, but becomes brown in the air at a rate depending upon the amount of impurities present.

This aniline oil has been used as an accelerator by simply pouring the oil into the compound when it has broken down on the hot mills. The vapors which came off from the mill were very injurious to the workmen, giving them aniline poisoning. The aniline acts upon the nervous system and even a small amount will turn the lips bluish and produce the effect of drunkenness, the patient becoming very pale and being affected with loss of appetite. The use of alcoholic liquors seems to be very harmful to one suffering from aniline poisoning.

Factories in which aniline was being used went to great expense to install ventilating systems with large hoods over the mills. It hastens the cure of rubber articles; makes vulcanization possible in a shorter time and also with the addition of less sulphur, which, of course, cuts down the possibility of blooming. Aniline is a solvent for sulphur and that may have its influence upon shortening the time of cure as we know reactions take place more rapidly in solutions or homogeneous systems than in heterogeneous ones. The use of aniline alone has been practically abandoned today in favor of those less harmful to the workmen and those existing in a form more easily handled. It serves, however, as a base for the production of some accelerators widely used at present.

One of the first ones to be used and one that is still widely used is the product which is formed when aniline and carbon bisulphide are brought together. The principal product which is formed is diphenylthiourea or thiocarbanilide. The reaction which takes place may be expressed thus:



$$\begin{array}{c} S \\ \| \\ C \\ \| \\ S \end{array} + \begin{array}{c} NH_2C_6H_5 \\ \\ NH_2C_6H_5 \end{array} \longrightarrow \begin{array}{c} NHC_6H_5 \\ | \\ C = S \\ | \\ NHC_6H_5 \end{array} + H_2S$$

To produce this substance in the pure

form, Gatterman gives the following procedure:

"A mixture of 40 grams of aniline, 50 grams of carbon bisulphide, and 10 grams of finely pulverized potassium hydroxide is gently boiled for three hours in a water bath in a flask provided with a reflux condenser. The excess of carbon bisulphide and alcohol is then distilled off, the residue treated with water, the crystals separating out are filtered off and washed first with water, then with dilute hydrochloric acid, and finally with water. To obtain a high degree of purity, it is crystallized from alcohol."

To produce the commercial product, all that is necessary is to place the mixture of aniline and carbon disulphide in large crocks or kettles in a warm place, where the escaping hydrogen sulphide will be carried away. The reaction will require perhaps thirty-six hours but it may be accelerated by the addition of sodium polysulphide. The yield is quantitative and there results a yellow, hard, crystalline mass. This is removed, pulverized, dried and is ready for use.

It should have a melting point of 154 deg. C. As an accelerator it is used in amounts from one-half to two per cent of the mixture.

In using this material, great care should be taken to reduce it to a fine powder. In grinding it tends to flake up, making it rather difficult to obtain the fine powder. If it is not reduced to a fine state of division, it will not be incorporated evenly in the rubber and will produce hard kernels of overcured rubber through the product.

This substance shows its greatest effect in accelerating cure at the beginning of the process and thus great care must be used in milling it for if the rolls get too warm, vulcanization will begin. This same substance, thiocarbanilide, may be obtained in the market under the name of "Excellerex."

Tetramethylenediamine is an accelerator which gives fair results in the final product, yet is not to be regarded as rapid in its actions as some of the others.

This substance is produced during the putrefaction of animal matter and is called putrescene. In this connection we might call attention to the results of Eaton and Grantham's experiments in the rapid curing of rubber. It will be remembered that they obtained a fast curing rubber when they coagulated by means which would allow of the putrefaction of some nitrogenous matter, and the thought arises that this accelerating action may be due to the formation of tetramethylenediamine.

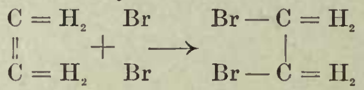
It may be produced on the commercial scale by first treating ethylalcohol with sulphuric acid, when the following reaction takes place:

$$C_2H_5OH + H_2SO_4 \longrightarrow C_2H_5SO_4H + HOH$$

with the formation of ethyl sulphuric acid. This substance then decomposes and yields ethylene thus:

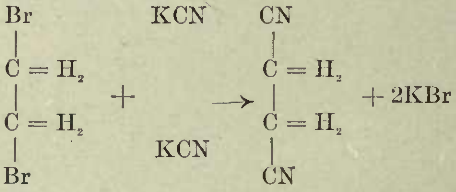
$$C_2H_5SO_4H \longrightarrow C_2H_4 + H_2SO_4$$

If the ethylene gas is then passed into bromine, the ethylene bromide is immediately formed.



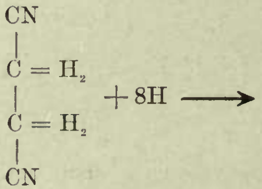
$$\begin{array}{lccr} C=H_2 & Br & & Br-C=H_2 \\ \| & + & \longrightarrow & | \\ C=H_2 & Br & & Br-C=H_2 \end{array}$$

Upon treating the ethylene bromide with potassium cyanide, the nitrile will be formed.



$$\begin{array}{lcccl} Br & KCN & & CN & \\ | & & & | & \\ C=H_2 & & & C=H_2 & \\ | & + & \longrightarrow & | & +2KBr \\ C=H_2 & & & C=H_2 & \\ | & KCN & & | & \\ Br & & & CN & \end{array}$$

This nitrile upon reduction with sodium in a hot alcoholic solution yields the tetramethylenediamine.



$$\begin{array}{lcc} CN & & \\ | & & \\ C=H_2 & & \\ | & +8H & \longrightarrow \\ C=H_2 & & \\ | & & \\ CN & & \end{array}$$

$H_2N \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot NH_2$

The substance is crystalline in nature and easily incorporated into the rubber.

Another product related to the one above is hexamethylenetetramine.

It is used in small quantities to disulphur musts and wines. Here it is called urotoropine. However, in this use it is in connection with sulphur as is also its use in the vulcanization of rubber. This substance is a derivative of formaldehyde and results when formaldehyde is treated with ammonia. Its reaction is shown in the following:

$$6HCOH + 4NH_3 \longrightarrow (CH_2)_6N_4 + 6HOH$$

F. Hermann has given the following method for the production of this substance. To the formalin in a closed receptacle, he added ammonium chloride in quantity sufficient to liberate enough ammonia to effect the above reaction with the amount of formalin taken, then enough caustic soda to free this ammonia from the ammonium salt. As rapidly as the ammonia is liberated, it will react with the formalin and produce hexamethylenetetramine. This substance finds a wide use today as an accelerator of vulcanization.

Paraphenylenediamine also is an accelerator quite largely employed in the rubber industry today and yet it is a very poisonous substance. Great care should be taken where it is used to guard the welfare of the workmen. It is regarded as one of the rapid accelerators. It may be made in several ways. First by the reduction of aminoazobenzene dissolved in aniline, with hydrogen sulphide or tin and hydrochloric acid. Second, by heating paradichlorobenzene or parachloraniline with ammonia in the presence of a copper salt. (Ger. Pat. 204408).

Beginning with aniline in the first method, the following steps are necessary according to Holleman.

Aniline treated with sodium nitrite in the presence of hydrochloric acid gives diazobenzenechloride, thus:

$$C_6H_5NH_2 + NaNO_2 + 2HCl \longrightarrow C_6H_5N{\cdot}NCl + 2HOH + NaCl$$

When this is treated with aniline the diazoaminobenzenechloride is produced.

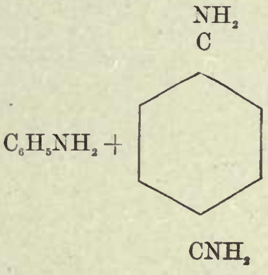
$$C_6H_5N{\cdot}N\ \vdots\, Cl + H\ \vdots\ NHC_6H_5 \longrightarrow C_6H_5N{\cdot}N{\cdot}NHC_6H_5 + HCl$$

One of the most characteristic reactions of these diazoaminobenzenes is their easy conversion into isomers, or the aminoazo compounds. This is best carried out by adding aniline hydrochloride to a solution of diazoaminobenzene in aniline and warming the mixture on a water bath.

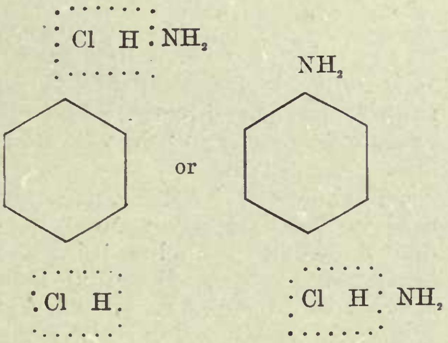
$$C_6H_5N{\cdot}N{\cdot}NHC_6H_5 \longrightarrow C_6H_5N{\cdot}N{\cdot}C_6H_4NH_2$$

Here the amino group is in the paraposition to the azo group. When this compound is reduced there results aniline and paraphenylenediamine.

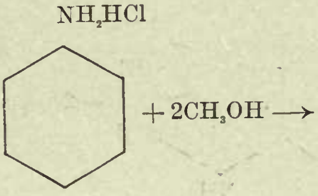
$$\underset{H_2}{C_6H_5N}\ \ \underset{H_2}{NC_6H_4NH_2} \longrightarrow$$

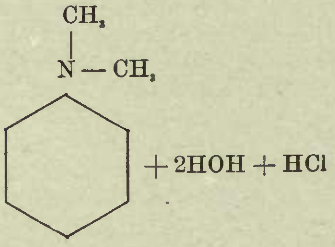


The second method is very simple as indicated above.



Under the trade name of "Accelerene," we find the substance paranitrosodimethylaniline. It may be made by heating aniline hydrochloride with methyl alcohol.

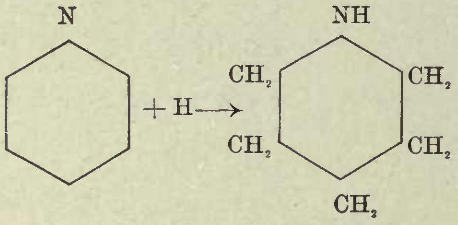




The hydrogen in the para-position of these dialkylamines is readily replaced by different groups. Thus the action of nitrous acid yields para-nitrosodimethylaniline. This substance possesses a greenish color and should have a melting point of about 85 deg. C.

Piperidine and some of its derivitives have been used, but, owing to the poisonous nature of these substances and their odor, they are not used to any great extent.

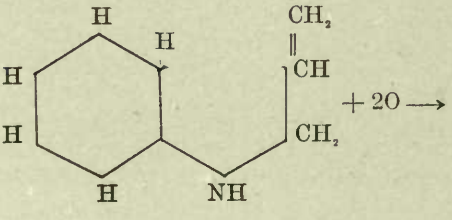
Piperidine is made by reducing pyridine with sodium and alcohol.

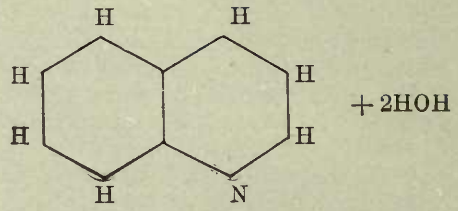


It is a liquid possessing an odor of pepper. It acts directly as an accelerator, however, upon vulcanization.

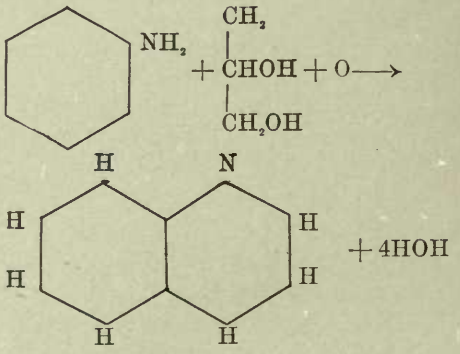
Quinoline and its derivatives are used in a satisfactory manner to a limited extent. Quinoline being the base of these, we shall outline only methods for the production of that substance. It is found in coal-tar and bone oil but is difficult to obtain from these sources.

Königs first synthesized it by passing allylaniline vapor over red hot lead oxide, when the following reaction took place.





Skraup's synthesis for quinoline as outlined by Perkin and Kipping is as follows: " Concentrated sulphuric acid 100 parts is gradually added to a mixture of aniline, 38 parts, and nitrobenzene, 24 parts, and glycerine, 120 parts, and the mixture is then very cautiously heated in a large flask (with reflux apparatus) on a sand bath; after the very violent reaction which soon sets in has subsided, the liquid is kept boiling for about four hours. It is then cooled, diluted with water, and the unchanged nitrobenzene separated by distillation with steam; soda is then added in excess to liberate the quinoline and the unchanged aniline from their sulphates and the mixture is again steam distilled. As these two bases cannot well be separated by fractional distillation, the whole of the aqueous distillate is acidified with sulphuric acid and sodium nitrite added until nitrous acid is present after shaking well. After heating, to convert the diazo salt into phenol, the solution is rendered alkaline with soda and again submitted to distillation with steam. The quinoline in the receiver is finally separated with the aid of a funnel and purified by fractional distillation." It is a liquid with a peculiar odor.



This, being a liquid, is not easily handled so it is converted into its sulphate and used most frequently thus. It is made by dissolving the quinoline in dilute sulphuric acid, when the sulphate $(C_9H_7N)_2H_2SO_4$ crystallizes out.

In addition to the ones mentioned above, many more have been tried; in fact, derivatives of all possible nitrogen compounds have been experimented with. Derivatives of the proteins of urea and ammonium compounds have all been recommended for this use.

Aldehyde ammonia, which is produced by passing dry ammonia gas into a solution of formalin, is a very good accelerator. It tends, however, to make the finished product harsh rather than of a velvety appearance.

Many substances which will accelerate must be discarded, for acceleration of cure alone is not a sufficient test for them. In addition to shortening the time for curing, they must also increase the physical properties of the rubber and thus reduce the deterioration of the finished products. So research along this line will continue even though at present we seem to be settling down to a few common accelerators.

CHAPTER XIV

The Manufacture and Use of Rubber Substitutes

In this chapter, we shall consider those materials which are used in the rubber industry along with rubber compounding, and the ones we shall mention contain no rubber in themselves, yet by their use, the actual amount of true rubber used may be reduced. The introduction of these materials must be done in such a way as not to be injurious to the final product, and likewise the substances themselves must not impair the physical properties of the articles.

The justification of the use of these materials in the beginning was especially to cut down the cost of the rubber goods by introducing some materials possessing properties like rubber yet which could be produced at a much smaller cost.

Such materials were found possible of production from many drying and even non-drying oils. It has been observed and known for many years that certain vegetable oils when exposed in a thin film to the air, or when in other words, were allowed to dry, formed a skin which possessed a few properties of rubber, such as toughtness and elasticity to a certain degree. What has really taken place is that the oil has been slowly taking up oxygen and has been converted into this semi-rubber like condition.

As early as 1846, Sacc produced a rubber like material by actually oxidizing linseed oil rapidly by the use of nitric acid. If linseed oil is heated in contact with air until it has oxidized to the state of a semi-solid mass, then nitric acid is added and the heating continued, it will finally arrive at such a state that when cooled in the air, a solid material results. This substance resembles rubber in appearance, is more or less elastic, softens in hot water, and is soluble in turpentine, carbon disulphide, and alkalies. When an alkaline solution of this product is treated with hydrochloric acid, it is precipitated unchanged. This property of oil of being changed by a process of oxidation in this manner is characteristic of drying oils in contrast to non-drying oils, which upon exposure to the air become rancid. This oxidized oil is known as "Oil Rubber," and because it is of commercial importance a more rapid method for its production was necessary. By the process mentioned, above, the oxidation takes place only at the surface of the oil, or where it comes in contact with the oxygen of the air.

To expose a greater surface of the oil to the oxidizing agent, a process has been patented whereby the hot, finely divided oil comes in contact with the air. This shortens the time of blowing the oil very materially. The final oxidation, however, is effected with nitric acid. The concentrated nitric acid is diluted with twice its volume of water and this and the thick blown oil are boiled together. The oil becomes thicker and thicker, but boiling is continued until a sample, when cold, will scarcely take the impress of a finger-nail. When this stage is reached, it is removed from the acid and is washed with boiling water until it is free from acid as determined by actual test. The oil rubber may now be formed into any desired shape and is ready for the market. It is used as an insulating material for electric wires.

Because of this property of oils to form addition products with oxygen, and due to the chemical analogy which exists between oxygen and sulphur, and the fact that sulphur is used in the vulcanization of rubber, it occurred to someone that it might be possible to cause the oils to form addition products with sulphur similar to those with oxygen. In other words it seemed possible to produce a " vulcanized oil " with properties more nearly like those of rubber than oil rubber possessed.

Thus it was found that by heating certain oils with sulphur, there resulted a substance possessing some degree of elasticity. This method of heating an oil with sulphur produces a dark colored product and this is referred to as " Brown or Black Substitute " or " Brown Factis." Its production resembles the " hot cure " process in the vulcanization of rubber itself. The oils most frequently used for this purpose are linseed, maize, cotton seed, and rape oil.

Many formulas and methods of procedure to produce Brown Substitute have been given from time to time, but we shall outline but three.

First, from linseed oil. If this oil is heated to 100 deg. C. and then from 5 to 10 per cent of sulphur is added and the temperature gradually raised to 130 deg. C., then allowed to cool back to 100 deg. C. and held at that temperature for some time, the vulcanizing will be complete. When the reaction is finished, the product is cooled on a smooth cold surface.

Second, if 8 gal. of corn oil are placed in a large boiler and rapidly brought to a temperature of 390 deg. F., during the heating a frothy curd will form over the surface of the oil which must be removed. During this heating, a current of hot air is blown through the oil which causes it to become more or less viscous. At this point, 0.20 lb. of sulphur, which has been previously melted, are added in the molten state. A vigorous reaction immediately begins and the whole mass froths up and is then poured into cooling boxes where it is stirred and allowed to cool. Black substitute then results.

The sulphur used here must be free from sulphurous acid and this fact must be determined by analysis. This black substitute may be softened by heat and cast into blocks and we find it in the industry largely in this form.

Another process for making Brown substitute from corn oil has been patented by William K. Leonard. This patent calls for 76 per cent of corn oil, 21 per cent of sulphur and 3 per cent of paraffin. The oil is placed in a kettle where it may be heated and when a temperature a little below 300 deg. F. is reached, the sulphur and paraffin are added. The temperature is still raised and at about 310 deg. F. the reaction begins and the source of heat is removed. The reaction will continue of its own accord, and in fact it being an exothermal reaction, the temperature will continue to rise often reaching 340 deg. F. during the process. The product is allowed to cool and is then ready to be incorporated into rubber compounds. (U. S. Pat. 615, 863.)

In 1846, Alexander Parkes mixed some linseed oil with from 20 to 40 per cent of sulphur monochloride and found that vulcanization would take place and a light-colored product result, what we call today " White Substitute " or " White Factis." This process is analogous to the " cold cure " which is used with rubber. It was found out later that if the oil was first dissolved in carbontetrachloride the reaction would take place in a great deal better manner, thus more nearly resembling the cold cure vulcanization.

Only small quantities of oil are treated at a time as the exothermal reaction causes such a rise in temperature that there results a big loss of the sulphur monochloride and the oil itself will carbonize. The monochloride used must be free from the dichloride of sulphur. This is very objectionable as it causes too violent a reaction with the result that the oil carbonizes and the product is burnt.

The amount of sulphur taken up by the oil varies from 5 to 15 per cent. The amount, however, will depend upon the degree of oxidation of the oil before the monochloride is added, that is, partially oxidized oils, or blown oils, will not take up as much sulphur. This same fact is true in regard to the making of Brown Factis, and that is the reason that the oils are first heated.

Henriques found that raw linseed oil requires at least thirty parts of sulphur monochloride to solidify when fresh while it requires only fifteen to eighteen parts when it has been heated for some hours at 200 deg. C. in contact with the air. He also observed that if the temperature is raised from 250 deg. to 300 deg., then 10 per cent of sulphur monochloride will suffice. All drying oils seem to behave in this same manner.

The same oils which are used for the production of Brown Factis may be employed for the production of the White. The raw oil is placed in shallow pans, which are constructed in such a way that air may be blown up through the heated oil in them. The oil is first heated to a temperature of 392 deg. F. to 464 deg. F. and the white scum which forms is removed; then air is blown up through the oil and the temperature raised to 572 deg. F. This partially oxidized oil is now run into large storing tanks or reservoirs where it is allowed to cool to ordinary temperature. The reason for this treatment, as was pointed out above, is to save sulphur monochloride, less of which is required with these oxidized oils.

A weighed quantity of this cold thick oil is placed in a large enameled boiler and stirring is begun. When the required amount of sulphur monochloride is added, white vapors will soon appear, indicating that the reaction has begun and their cessation will serve as an indication of the completion of the reaction. The mixture of oil and monochloride is maintained at a temperature of 131 to 140 deg. F. The factis is removed and placed upon nets, which allow the escape of the odor of the sulphur monochloride. The product is almost colorless and is not affected by boiling with dilute acids and alkalies in distinction from the brown factis which is soluble in alkalies.

William K. Leonard has also patented a process for the production of the white substitute. According to his patent, 64 per cent of corn oil and 13 per cent of castor oil are thoroughly mixed and then 21 per cent of the entire mass of sulphur monochloride, 0.5 per cent of naphtha and 1.5 per cent of oxide of magnesia are added. The reaction immediately begins and the temperature tends to rise, but when the reaction is completed and the whole mass allowed to cool, a white spongy product will result. (U. S. Pat. 615,864.)

For the production of a white factis from linseed oil, Nicolaus Reif has patented a form of apparatus for mixing the oil and sulphur monochloride under pressure in such a manner that the whole mass is mixed by a rotary movement and expressed from the apparatus by a similar movement thus reducing the mixture to a flake-like condition. (U. S. Pat. 1,006,274.)

Henriques has prepared a table showing the production of White Factis from different oils:

Linseed oil congeals with 30 parts sulphur monochloride, but not with 25 parts.

Poppy oil congeals with 35 parts sulphur monochloride, but not with 30 parts.

Rape oil congeals with 25 parts sulphur monochloride, but not with 20 parts.

Cotton seed oil congeals with 45 parts sulphur monochloride, but not with 40 parts.

Olive oil congeals with 25 parts sulphur monochloride, but not with 20 parts.

Castor oil congeals with 20 parts sulphur monochloride, but not with 18 parts.

It is really remarkable to what extent factis may be used in rubber without affecting the elastic properties of the rubber, in fact it may be added up to a proportion of 1:1. This is due to the mechanical consistency of factis, which possesses compressile elasticity, but is destitute of tensile strength. So by its addition we may sacrifice tensile strength, but not impair springiness.

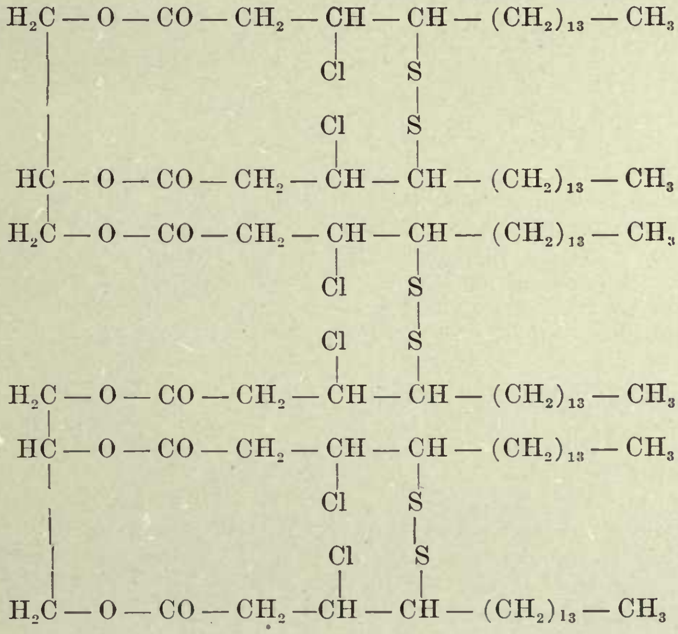
The specific gravity of factis varies between 0.98 and 1.02 and it is the only material by which floating goods may be cheapened.

Brown Factis often contains paraffin wax or heavy petroleum fractions, both of which are added to the oil before it is vulcanized. Generally we are safe in saying that the less there is of unvulcanized oil in a substitute the better it is, for the free oils have a tendency to shorten the life of the goods. The best White Factises are those which are driest and least coherent in the ground state and the combined per cents of sulphur and chlorine should not exceed twenty.

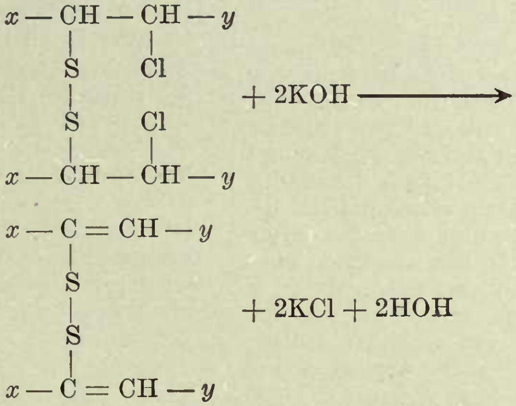
The free sulphur content must be known whenever a factis is used in compounding for this will have its influence upon the amount of sulphur to be added.

The exact chemistry of the production of these substitutes is not known, yet the possible steps may be indicated.

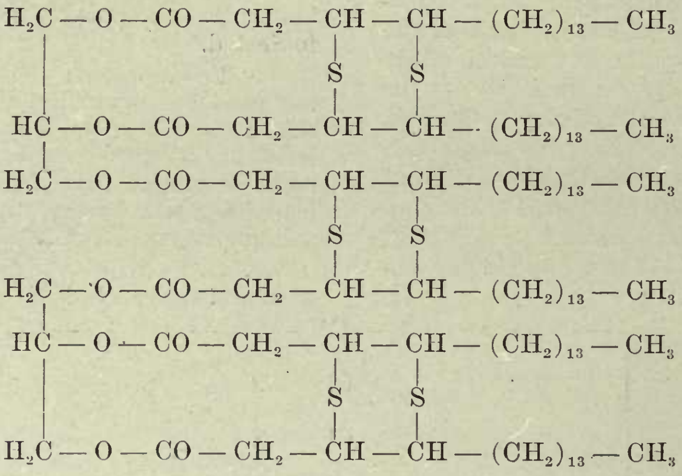
We do know that the oils which are used are glycerides of the fatty acids; therefore we may draw the following picture where two molecules of one of these glycerides are bound together by three molecules of sulphur monochloride S_2Cl_2.



When this White Factis is treated with a boiling alcoholic solution of N/2 potassium hydroxide, it is saponified and the sulphur atoms will remain bound to the fatty acids.



The Brown Factis may then be represented in the following manner:



From these formulas it will be seen why a partially oxidized oil will require less sulphur or sulphur monochloride for the oxygen will go into the substance in the place of these.

The substances which have been treated above are substitutes only in the sense that by their use, the actual amount of rubber taken may be reduced, but we may mention a few substances which have been made that are substitutes for rubber itself. In other words, they may be made up into articles in which rubber has been used before. Such a substance is Sulphuretted Hydrocellulose. It was discovered by Sthamer and is made by treating finely ground hydrocellulose with enough hydrochloric acid of 24 deg. Baumé at ordinary temperature to form a thin paste of the nature of a solution. To this sulphur monochloride is added and the whole mass stirred. After some time the fluid turns turbid and when placed in cold water, the sulphuretted hydrocellulose settles to the bottom in one large mass. It is removed and placed upon a screen where it is allowed to drain and the excess acid thus recovered, then washed with water until free from the acid. This substance is insoluble in all known solvents.

When this material is compounded with rubber and then subjected to vulcanization, it will decompose and give up its sulphur to the rubber which in turn is cured. It seems that such a substance might find more application in the rubber industry.

Several patents have been taken out by Julius Stockhausen for the making of a substitute for india rubber. In one of these, 125 grams of gelatin are dissolved in 125 grams of glycerine and this then mixed with 5 to 20 grams of sulphur, 20 grams of camphor, and 15 to 20 grams of colophony. This mixture is heated for a long time and there is added to it 10 to 20 grams of formaldehyde or 3 to 10 grams of sodium bichromate. This produces an elastic and plastic substance.

He has also patented the following formula: 125 grams of powdered gelatin or agar-agar are dissolved in 125 grams of crude glycerine, 25 deg. Baumé at 70 deg. C. Then 15 grams of tar and 25 grams of naphthalene are added and finally 20 grams of 4 per cent formaldehyde are used for hardening. This substance may then be cast into molds of any desired shape.

We might go on and enumerate many, many such substances which have appeared from time to time, but it hardly seems advisable.

Within the last few years, the practice of adding the bitumens and pitches has become very common. The Trinidad and Syrian asphaltum has been used for some time in the insulating of cables, but now these and bitumen in the form of mineral rubber are being used in compounds even as high as 50 per cent of the rubber content. These mineral rubbers are many in number and are made from soft natural bitumens or from blown petroleum residues. In the trade, we find the substances M.R.X. and Rubrax as examples of these materials. The real value of any of these must be determined by actual use and their properties determined by mixing and vulcanizing. A great deal has been said and written of late in regard to the different effects produced by high and low softening point products. We do not wish to enter into that controversy here, but it has been claimed that high softening point mineral rubber produces a high tensile rubber but one with low resiliency, while low softening point material produces a low tensile but good resiliency. Thus we have an excuse for the manufacture of both grades.

Some resins of natural occurrence are used as rubber substitutes and we simply wish to mention rosin, shellac, copal, acroides, sandarac, dammar which are regarded as resins proper. Then, we find growing in the tropical regions plants which produce a resin containing also a certain percent of rubber itself. These substances appear under the names of Jelutong, Palembang, Pontianak and Dead Borneo. These materials all find a limited use in the rubber industry.

CHAPTER XV

Theories of Vulcanization

The term vulcanization is derived from "Vulcan," the Roman fire god, its connection with regard to rubber being therefore the heat which causes rubber when mixed with sulphur, to assume entirely different physical and chemical properties.

There are two general methods of vulcanization, namely, what is known as the "cold cure" and the "hot cure vulcanization." The former is effected by the use of a sulphur monochloride solution, which acts upon the rubber, and as it is a surface action, it may be employed only with very thin articles. This method is also allowed to take place by placing the articles to be vulcanized in the vapors of sulphur monochloride.

The credit for this process belongs to Parkes, who, in 1846, dipped thin strips of caoutchouc, for different lengths of time, in to a solution of 100 parts of carbon disulphide and 2.5 parts of sulphur monochloride. After dipping these strips, he quickly dried them at 78 deg. F. and then washed them in warm water. The process has been modified somewhat since his day but the essential features were known to him.

The credit for the "hot vulcanization" should be divided between Hancock and Goodyear, who independently discovered that rubber, when heated in contact with sulphur, changes its properties very materially.

They arrived at this conclusion, however, by slightly different means. Hancock in 1843 patented a process for vulcanization whereby he subjected sheets of rubber to the action of molten sulphur heated to a temperature of 284 deg. to 302 deg. F., when the rubber took up 10 to 15 per cent of sulphur. Of course, these sheets had a great tendency to bloom, so he washed them with a solution of soda. At the same time Hancock was trying these experiments, Goodyear was working along the same lines, only he was mixing the sulphur into the rubber, until he had a homogeneous mixture which he subjected to a high temperature. Of course, the two results were similar, but Goodyear's method being, in many ways, the easiest to control, is the one which has survived. Gerard found that it was possible to effect vulcanization by subjecting the rubber for three hours, under a pressure of four atmospheres in a solution of calcium pentasulphide, to a temperature of 265 deg. F. The articles are then removed and washed with warm water. They are well cured and will possess a velvety appearance. The length of time they must remain in such a bath, of course, is determined by the thickness of the articles to be vulcanized.

Victor Henri in 1909-10, first exposed rubber to the action of ultra-violet rays and found that it underwent a kind of oxidation. Later it was found that, if a solution of rubber containing sulphur was subjected to the ultra-violet rays, the whole mass became thick and of a gelatinous nature, and by test showed combined sulphur. These vulcanized solutions may be used for rubberized cloth, used as cements. for rubberizing leather, or used in repair work of all kinds.

The French have called this process "Cuisson" and the Germans "burning" but today "vulcanization" seems to be the accepted term.

Inasmuch as the hot vulcanization process is dependent upon the tem-

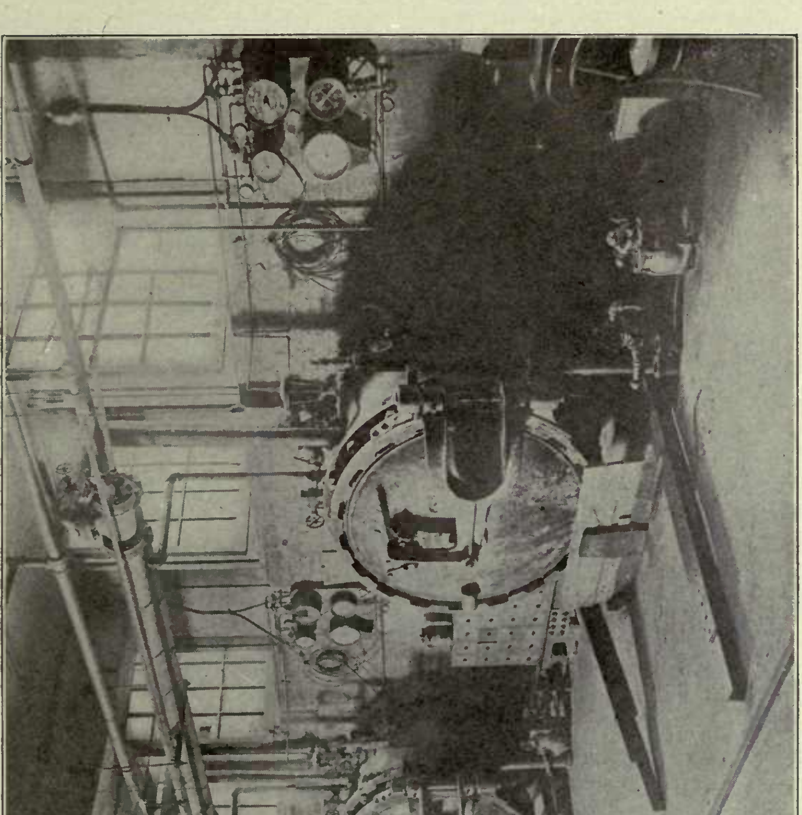
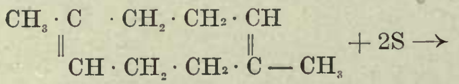


Fig. 32—Battery of Horizontal Vulcanizers in a Large Rubber Factory

perature to which the rubber is subjected, as will be pointed out later, it is very essential that, during vulcanization, a close watch is kept of the temperature. A few years ago, although it was known that it was the temperature which effected the change, yet because the heat was derived from steam, which was measured in pounds per square inch, steam pressure was the method of control used in vulcanizing rubber. This led to many very bad results. For instance, in a vulcanizer, you might have the desired pressure of 45 pounds indicated by your pressure gage and yet there might be pocketed air at some place in the heater which is not at the desired temperature and faulty goods would result.

There is no excuse for such trouble today when it is possible to obtain automatic, self-recording thermometers like those put out by the C. J. Tagliabue Co. or those of the Bristol Co.



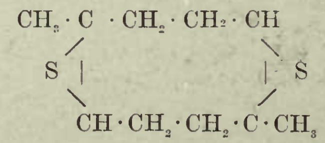
$$\begin{array}{l} CH_3\cdot C \quad \cdot CH_2\cdot CH_2\cdot CH \\ \quad \| \qquad\qquad\qquad\qquad \| \qquad\quad + 2S \rightarrow \\ \quad CH\cdot CH_2\cdot CH_2\cdot C — CH_3 \end{array}$$

What really takes place during vulcanization, or in other words, the chemistry of what causes this marked change in the properties of the rubber, was not investigated to any great extent until 1902 to 1910. Up to this time, the process had been regarded as purely a chemical phenomenon.

Weber's Theory

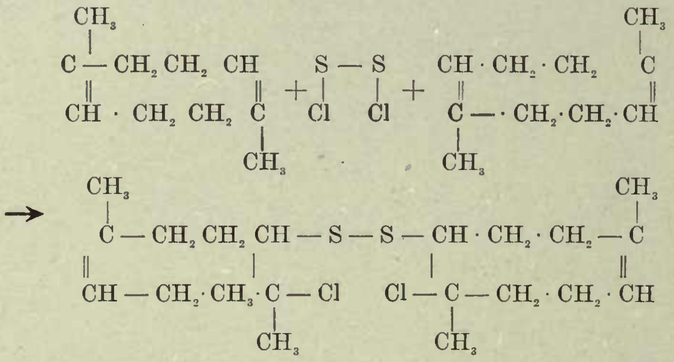
The early work of a scientific nature along this line was conducted by Weber and he laid down theories of vulcanization which later came in for their amount of criticism. We shall here bring forth the main points which he developed.

Previous to this time the impression had existed that when rubber was mixed with sulphur and then heated, substitution took place. Weber showed conclusively that this was incorrect for he pointed out that if this were true, an immense volume of hydrogen sulphide must be produced, which is contrary to our working experience. Thus the substitution theory was abandoned and in its stead, Weber recommended the addition theory. According to that theory if we accept the formula for caoutchouc as recommended by Harries, we have a compound with double bonds at which points addition is possible.



$$\begin{array}{l} CH_3\cdot C \quad \cdot CH_2\cdot CH_2\cdot CH \\ \quad\; / \qquad\qquad\qquad\quad \backslash \\ S \;\; | \qquad\qquad\qquad\quad | \;\; S \\ \quad\; \backslash \qquad\qquad\qquad\quad / \\ \quad CH\cdot CH_2\cdot CH_2\cdot C\cdot CH_3 \end{array}$$

This will stand for rubber completely saturated or hard rubber which has a constant per cent of sulphur of approximately 32. This same reaction takes place in the cold cure, only Hinrichsen has pointed out that the reaction undoubtedly takes place between two such molecules thus:



$$\begin{array}{l} CH_3 \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad CH_3 \\ \;| \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad | \\ C — CH_2\,CH_2 \;\; CH \qquad S — S \qquad CH\cdot CH_2\cdot CH_2 \qquad C \\ \| \qquad\qquad\qquad\quad \| + | \qquad | \;+\; \| \qquad\qquad\qquad\qquad \| \\ CH \cdot CH_2\,CH_2 \;\; C \qquad Cl \qquad Cl \qquad C — \cdot CH_2\cdot CH_2\cdot CH \\ \qquad\qquad\qquad\quad | \qquad\qquad\qquad\qquad | \\ \qquad\qquad\qquad CH_3 \qquad\qquad\qquad\quad CH_3 \end{array}$$

$$\begin{array}{l} \quad CH_3 \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad CH_3 \\ \rightarrow \;\; | \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad | \\ \quad C — CH_2\,CH_2\;CH — S — S — CH\cdot CH_2\cdot CH_2 — C \\ \quad \| \qquad\qquad\qquad | \qquad\qquad\qquad | \qquad\qquad\qquad\quad \| \\ \quad CH — CH_2\cdot CH_3\cdot C — Cl \qquad Cl — C — CH_2\cdot CH_2\cdot CH \\ \qquad\qquad\qquad\qquad\quad | \qquad\qquad\quad | \\ \qquad\qquad\qquad\qquad CH_3 \qquad\qquad CH_3 \end{array}$$

Weber pointed out that the amount of sulphur which actually entered into vulcanization was dependent to some extent on many factors, most important of these, however, being the amount of sulphur really present and capable of entering into the reaction, and second the temperature at which the vulcanization was taking place, and third the length of time it was subjected to this temperature. By varying these conditions, we obtain different degrees of vulcanization ranging from a soft consistency up to hard rubber for ebonite.

In order to have some scale for comparing this degree of vulcanization, Weber suggested the term " coefficient of vulcanization." That is, in all grades of cured rubber, we have sulphur in at least three modifications. There is " total sulphur," " free sulphur " and " combined sulphur." the latter being the amount of sulphur which is in combination with caoutchouc. It is the ratio of this sulphur to the total amount of rubber present in the finished product which is called the coefficient of vulcanization.

The unfortunate thing about the use of this is the fact that the same coefficient of vulcanization with different grades of rubber produces entirely different results, and, in fact, different results in the same rubber if it is handled in different ways. Weber came to the conclusion that this range of vulcanization from soft rubber to ebonite could be represented by the formation of ten sulphur compounds with caoutchouc, the lowest having a formula of $(C_{10}H_{16})_{10}\ S_2$ and the highest expressed by the formula $C_{10}H_{16}S_2$. As proof of this he found that when determining the combined sulphur in samples cured for different lengths of time with an excess of sulphur present and then plotting the combined sulphur with its per cent on one axis and time expressed on the other, he obtained a broken curve which he took as evidence of a chemical change taking place. These are the points adduced by Weber in support of his theory. We shall now give a brief review of the theory of W. Oswald concerning vulcanization.

Oswald's Theory

W. Oswald was of the opinion that vulcanization might be explained better upon the grounds of the physicochemical theory of absorption dealing with colloids than upon Weber's purely chemical theory.

This theory of Oswald's is found in Z. Chem. Ind. Kolloide, 1910, 6, 136-155, as it may be applied to vulcanization, and he points out the following facts in support of his theory:

First—Regardless of the amount of sulphur added to rubber, whether large or small, there always remains after vulcanization a certain amount of it in the free state, while the chemical theory would require, that if small in amount, it should all be combined.

Second—If vulcanized rubber is extracted with petroleum spirit, sulphur will continue to be removed as long as any remains in the rubber and this same is true of unvulcanized rubber only the sulphur is extracted more rapidly.

Third—The adsorption of sulphur by rubber is always additive.

Fourth—A continuous series of additive products is formed and yet the amount of sulphur in the series does not conform to the law of multiple proportions.

Fifth—The amount of adsorbed sulphur will depend upon the previous mechanical working of the rubber. The more the mechanical working, the greater the amount of surface produced and thus the greater the adsorptive power of the rubber.

Sixth—The adsorption increases with rise of temperature and conforms more nearly to what should be expected from a physico-chemical adsorption than from a chemical change alone.

Seventh—The adsorption of sulphur is not regular as the sulphur curve shows changes in direction.

Eighth—The adsorbtion of sulphur proceeds more nearly according to the adsorbtion formula than to any chemical one. That is,

$$\frac{x}{a} = kc^m$$

Where x = amt. of adsorbed substance,
a = amt. of adsorbent.
c = initial concentration of substance which is adsorbed.
k and m are constants.

From these facts, Oswald concludes

that vulcanization is to be considered as an adsorption of the sulphur by the rubber. Hinrichsen and E. Kindscher studied the reaction which takes place during cold vulcanization (Z. Chem. Ind. Kolloids, 1910, 4). They prepared a solution of rubber in benzine, using a known quantity of rubber. To this they added a known quantity of sulphur monochloride dissolved in benzine and allowed the two to react for three weeks. At the end of this time, they determined the amount of unchanged sulphur monochloride and by difference they ascertained the amount which had reacted with the known amount of rubber. They came to the conclusion that for a certain amount of rubber, the amount of adsorbed monochloride is constant and is independent of the amount taken. They then calculated a formula for this final compound which they wrote as indicated above $(C_{10}H_{16})_2 S_2 Cl_2$. This work seems to favor, therefore, the idea of a chemical change during vulcanization but Oswald pointed out that this simply represented the maximum amount of adsorbed sulphur and represented that part of the sulphur curve which was parallel to the axis.

These same men later carried out the following test with hot vulcanization. They prepared a solution of rubber in cumene of such a concentration that each 100 c.c. of the solution contained two grams of rubber. To several such amounts they added 1, 2, 3, 4, 5, 6, 7 and 8 grams of sulphur respectively. The mixtures were then all subjected to a temperature of 170 deg. C., while being agitated by carbon dioxide. In each case, the product which resulted did not contain more than 32 per cent of sulphur and therefore agreed with Weber's formula of $C_{10}H_{16} S_2$ showing that here perhaps is a chemical compound capable, therefore, of being represented by a formula.

Following the appearance of Oswald's theory we find a great deal of investigation and discussion along this line.

Spence's Experiment

Spence and his workers in this country did a great deal of work on this theory of vulcanization. For instance, they studied the velocity with which free sulphur is extracted from vulcanized rubber by use of hot acetone and came to the conclusion that the last portions of free sulphur are removed very slowly but that a point is reached where no more sulphur may be removed. Therefore, in contradiction to Oswald's theory, they claimed that a definite amount of sulphur had really entered into chemical union with the rubber during vulcanisation. They do, however, agree with Oswald in that they believe that the free sulphur may be adsorbed.

Reversability of Vulcanization Process

P. Bary and L. Weydert (Comptes Rend., 1911, 153, 676-679) did a piece of work to prove that the process which takes place during vulcanization was one which might be reversed. They extracted some vulcanized rubber with hot acetone until all free sulphur was removed and then heated the extracted rubber for eight hours at 145 deg. C. in carbon dioxide. Following this they extracted again with hot acetone and repeated the previous treatment twice more with the result that the final amount of combined sulphur was less than in the original sample. Therefore, they felt that they had reversed the process of vulcanization to a certain extent. This is a very important point in the controversy for if vulcanization may be reversed, it lends great weight to the adsorption theory, while, on the other hand, if it is impossible to reverse the process, then it argues in favor of Weber's theory. They were also of the opinion that during vulcanization, the rubber itself was depolymerized.

Migration of Sulphur in Rubber

H. Skellon has carried out some experiments dealing with the migration of sulphur in rubber during vulcanization. He superimposed two sheets of rubber containing different percentages of sulphur and then subjected them to vulcanization conditions and came to the following conclusions:

That migration takes place either upward or downward with equal facility.

That equilibrium is very quickly arrived at in the two sheets during vulcanization, and then the concentration of the free sulphur in the rubber is the same in the two sheets.

That the evidence points to the fact that vulcanization is most probably

(1) Melting of the sulphur;

(2) Solution of the sulphur in rubber;

(3) Slow combination of the sulphur with the rubber.

Skellon made a study of the effect of the polyprene sulphide during vulcanization and came to the following conclusions:

Let us picture vulcanization to be represented by the following reaction

$$(C_{10}H_{16})_n + NS_2 <\!\!-\!\!> NC_{10}H_{16}S_2$$

If this is true, we should expect that during vulcanization, the ratio of rubber to sulphur remains the same and therefore the reaction should proceed at the same rate of speed, but by actual experiment, this is found not to be the case. The speed of vulcanization is decreased as the process goes on. This is explained by Skellon to be due to the fact that sulphur is more soluble in polyprene sulphide than in rubber and therefore the law of partition comes in and we actually have some of the sulphur extracted from the rubber by the sulphide which is formed, hence more sulphur will be dissolved by it and the last stages of the cure will proceed very slowly as a result of this.

Researches by Loewen

H. Loewen has carried out a very interesting experiment favoring the idea that the process of vulcanization consists in the sulphur's first dissolving in the rubber and then combining chemically with it, in contrast to the adsorption theory of Oswald.

To study this phenomenon, he placed a small amount of rubber with 10 per cent of its weight of sulphur on a microscope slide and placed over it a cover glass. This slide he then subjected to a temperature of 130 deg to 140 deg. C., and at regular intervals made microscopic examinations of it.

At first the sulphur melted and the globules could be seen through the rubber itself, later the globules distributed themselves throughout the whole mass and by continued heating, the whole mass became clear or transparent, but he observed further that as this cooled, it became cloudy due to the separating out of the globules of rubber which, as we know, change back in cooling to the rhombic form. Then, again, if the slide is heated until upon cooling it still remains clear, then when the excess sulphur does separate it will do so in the crystalline form and not appear as globules first thus resembling solutions. He also found that sulphur is more soluble the higher the degree of vulcanization and calls attention to the fact that hard rubber does not tend to bloom even though it may have a large per cent of free sulphur. This is explained, therefore, on the ground that the sulphur, being more soluble, here remains in solution. He then placed some rubber alone on a slide and placed over it the cover glass and around the edges of the rubber he placed molten sulphur. After regular intervals of heating, he would examine it with the microscope and found that the sulphur diffused into the rubber to some distance as would be expected during solution of one in the other.

These experiments led Loewen to the firm belief that vulcanization was truly a chemical process. (Gummi-Zeit. 1913, 27, 1301-1302.)

Vulcanization and Viscosity

Dr. Gustave Bernstein in a report before the Rubber Congress, held in London, 1914, showed how he had studied vulcanization from the standpoint of viscosity. He is of the opinion that rubber must be depolymerized before it can enter into chemical change, that is, it must change physically from $(C_{10}H_{16})_n$ to $NC_{10}H_{16}$. All of the agents which will depolmerize rubber will also reduce its viscosity. He also observed that the viscosity of all completely depolymerized rubber was the same. He also called attention to the fact that all the physical agents that bring about depolymerization, cause a vulcanization action to take place when the rubber is mixed with sulphur. An example of this is seen when a solution of rubber and sulphur is exposed to the ultra-violet rays. Its viscosity immediately increases. If this is true, then our vulcanization is to be explained upon the ground that the heat first depolymerizes the rubber and then the sulphur repolymerizes it.

In support of this theory, he points out the fact that while mixing sulphur and rubber on the rolls at a temperature not exceeding 80 deg. C, vulcanization took place and by analysis, 0.8 per cent of combined sulphur was found, while upon heating the same mixture in an oven at 80 deg. C for the same length of time no combined sulphur was found.

The conclusion to be drawn is that the mechanical work assisted the depolymerization of the rubber and the sulphur then entered into combination. Then if this be true, the sulphur must act partly at least in the capacity of a catalytic agent. That this is true follows from the work of Helbronner where he found that actinic light had really vulcanized the solution of rubber and sulphur and yet the amount of combined sulphur was only 0.6 per cent. This fact is still borne out by the addition of a small amount of sulphur to aid in the polymerization of isoprene to produce synthetic rubber by the Badische Anilin process. The rubber obtained by this process is polymerized more highly than the natural rubber.

He therefore draws the following conclusions: first, that what we call vulcanization is a repolymerization; second, smaller quantities of sulphur than are ordinarily used are capable of effecting this change; third, the amount of combined sulphur is not necessarily a measure of the degree of vulcanization as claimed by C. O. Weber.

The following idea has also been brought forward. As we know certain physical agencies have the power of lowering the viscosity of rubber and this points to its depolymerization. However, the action of physical agencies, like ultra-violet rays, upon sulphur in solution is to polymerize it and thus make it into an insoluble colloidal form. Therefore, vulcanization is first depolymerization of the rubber and at the same time polymerization of the sulphur and then we may think of the depolymerized rubber as adsorbing the colloidal sulphur.

Upon this theory we might explain the deterioration of rubber under the influence of certain physical agencies as due to the continuation of the depolymerization of the rubber and the increased polymerization of the sulphur.

Ostromislensky's Theory

I. I. Ostromislensky has recently advanced what may be looked upon as a combination theory made up of the two others. He suggested that vulcanization consisted first in a small amount of sulphur forming a derivative with the caoutchouc which may be regarded as the vulcanizing substance, second this substance is then adsorbed by the remaining rubber and the whole mass is regarded as vulcanized. Thus it will be seen that it is first a chemical change and then an adsorptive process. It is in this state of reasoning and theorizing that we find ourselves today.

From work carried out in this laboratory, we have come to the belief of Spence that it is a chemical change and that when accurate determinations of the combined sulphur are made on samples taken at short intervals of time, the sulphur curve will become a smooth one without the kinks in it which Weber found, and may thus be looked upon as a true chemical change.

CHAPTER XVI

Methods of Reclaiming Rubber

In this section, we shall consider the different ways in which rubber which has been once used may be treated and thus returned to compounds.

This of course includes a great many different processes because of the great variety of compounds or stocks which furnish the material to be reclaimed and then too the great number of stocks into which the shoddy may be worked.

We shall have therefore as raw material which is to be reclaimed, first, unvulcanized stock in the form of trimmings. This may have in it fabric, mineral fillers and its free sulphur. Second, the vulcanized stock, ranging in degree of vulcanization from soft cure up to hard cure or ebonite. These materials may contain fabric, fillers, and even metal as we find the metal beads in tires, free sulphur and substitutes. Third, we have hard rubber waste itself.

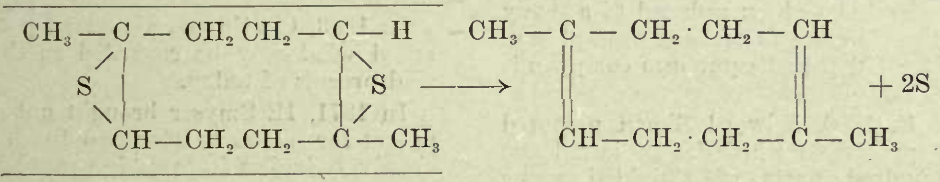
The first class of material very seldom comes into the hands of the reclaimer proper for being unvulcanized. All that is necessary is to treat the waste with a rubber solvent like naphtha. A great deal of the waste does not contain even fabric, but simply the rubber plus the sulphur and mineral fillers, and when the solution is effected, the naphtha solution is wrung out of the fabric if it is present, and if absent it is decanted from the mineral matter. The solvent is then evaporated and the rubber is thus reclaimed. This is a very simple process, and, although strictly speaking it is a form of reclaiming, yet it is one that is not regarded as such in the reclaiming industry.

The big problem that confronts the reclaimer is the handling of the second class of materials, namely that which has been vulcanized and thus had some of its chemical and physical properties changed by some of the sulphur having entered into chemical union with the caoutchouc.

Therefore every man when he approaches the problem does so with the idea that he will be able to find a process whereby the original hydrocarbon will be found again in a form capable of the same degree of vulcanization that it possessed before it ever went into a rubber compound. In fact he tries to split off the sulphur atoms in the vulcanized molecule and thus go back to the unsaturated hydrocarbon.

This might be represented as the reverse of the action which took place during vulcanization and might be called devulcanization.

This would represent the process in the case of ebonite. That this goal has never been reached and that it is not probable that it will be reached seems apparent today.



The formula $C_{10}H_{16}S_2$ as we have mentioned before represents hard rubber, yet the rubber which has been subjected to reclaiming contains much less combined sulphur than this formula indicates.

The above formula contains approximately 32 per cent of sulphur, while the material used by the reclaimer will average about 3 per cent or even less. It would appear therefore that a large part of the rubber is not vulcanized and that all that would be necessary to obtain the unvulcanized rubber would be to treat the product with a suitable solvent, then evaporate it off and the rubber would thus be obtained. But this is not the case, for the combined sulphur and the product in which it exists are very securely bounded and held together.

However, to effect the above mentioned change many patents have from time to time appeared, many of which have never been put into practice and many of which have been allowed to lapse. We shall simply mention some of these and when doing so will classify them as to whether they are purely mechanical processes or chemical ones. The latter may be either "Acid" or "Alkali."

Devulcanization Processes

In 1857, Conrad Poppenhusen and Ludwig Held suspended finely divided rubber in different solvents and then conducted into this mixture dry ammoniacal gas. The gas is absorbed and the gum swells, the whole mass becomes viscid, and this material is then suitable to be used in new compounds.

One of the oldest methods was presented by Hiram L. Hall in 1858. In this process the vulcanized rubber was boiled up with water in a caldron after it had been reduced to a finely divided state to make it semi-plastic. It could then be put into compounds again.

In 1860, Edward Simon patented a process in which he subjected one hundred parts of shredded waste vulcanized India rubber and two parts of chloride of lime to an open heat at a temperature of 1000 deg. to 1100 deg. F. The rubber melted and during constant stirring the sulphur was distilled out. The plastic mass which remained could then be worked into new stocks.

In 1861, John Murphy took out a patent for the reclaiming of rubber whereby the old rubber was mixed with sulphur and vulcanized until it formed hard stock. This was then formed hard stock. This was reduced to a powder and then mixed with unvulcanized gum and made into whatever form was desired and this vulcanized. This was a peculiar manner, to say the least, of using waste rubber.

In the same year, Charles McBurney patented the idea that by mixing old vulcanized rubber which had been reduced to a fine state with oils like pine or rosin oil, cottonseed oil, olive oil, castor oil, palm oil, or cocoanut oil, and allowing it to stand for several hours, then by adding raw rubber and the necessary fillers for which the product is intended, the material may be all incorporated on a mill and vulcanized. It thus affords a way of using old rubber.

Thomas J. Mayall in 1862 proposed that vulcanized rubber waste might be rendered fit for use again by grinding the material to a fine powder. He then made up a batch composed of five-eighths of this old rubber and three-eighths of a vegetable oil or pine oils and mixed them thoroughly on a mill. This material was then subjected to a gentle heat.

In 1863, Alfred Ford patented in England a process in which the old rubber is boiled with a strong solution of alkali; the material is then powdered and placed in moulds which are subjected to a hydraulic pressure and heat of ordinary vulcanization by which the whole will be agglutinated.

In 1863, Charles H. Hayward patented what may be regarded as the acid process of today.

In 1871, H. Smyser brought out a patent for the using of old rubber by simply reducing it to a fine powder on a grindstone and then incorporating this dust into a new compound.

In 1881, N. C. Mitchell defended by patent what are known as the acid processes.

He reduced the rubber to be

treated to a fine state of division, then placed it in a tight steam box in which a steam pressure of from 50 to 75 lb. could be maintained. Into this box containing the rubber he placed sulphuric acid or muriatic acid of varying strength, depending upon the grade of compound to be treated. Then the whole was closed and the steam turned on for from one to five hours. The rubber was then removed, washed and dried. This treatment of course removes fabric from the compound as well as mineral fillers which are used.

McDermott in 1882 modified the Mitchell acid process a little by adding alone with the charge of acid and rubber some manganese dioxide and a solution of potassium bichromate. Then he subjected the whole to steam under pressure, the result being practically the same.

In 1883, A. W. Kent patented an apparatus for the washing of ground rubber on a sieve, thus allowing the dirt and sand to be washed away, also the fiber, and allowing simply the vulcanized rubber with its fillers to remain. This is dried and as such is mixed with new compounds.

In 1883, John L. Chadwick patented a process for removing both cotton and wool fabric from vulcanized rubber. The scrap is first immersed in muriatic acid of 10 deg. Baumé and then heated to from 200 deg. to 212 deg. F. This continues for a couple of hours, when the cotton is destroyed. The material is then wrung out of the acid and passed through a wool picker. Not all of the wool is removed in this way, so it is then placed in a 22 deg. Baumé solution of caustic soda. Before this all the acid must be removed by washing. When removed from the soda solution and washed, it is in a good workable form.

In 1884, J. J. Montgomery subjected vulcanized rubber to the action of hydrocarbons obtained from petroleum, that have boiling points around 400 deg. to 450 deg. F., at a temperature of 350 deg. F. The rubber becomes a doughy or plastic mass from which the oils are removed by heat.

In 1890, N. C. Mitchell patented a new modification in which the rubber after it had been ground and washed is heated with steam in the presence of calcium sulphide to which has been added some heavy petroleum which keeps the rubber in a moist condition.

Maximilien Gerber in 1894 protected his process of reclaiming by a patent whereby the rubber scrap is heated in a double bottomed closed vessel with a solvent for the gum along with a metal, in the finely divided condition, which has a great affinity for sulphur. Such metals are iron, tin, lead, zinc, mercury, etc., and the solvent being benzine, carbon tetrachloride and the like.

The charge is heated to from 139 deg. to 144 deg. C. for about eight hours; then it is allowed to stand in a receiver for twenty-four hours, when the sulphides and fillers will have settled out and the rubber solution is decanted. The rubber is obtained by evaporating the solvent or as a solution is used to waterproof cloth.

In 1899, A. H. Marks patented what is known as the alkali process. By this method the ground rubber waste is brought to a temperature of 344 deg. to 370 deg. F. in a 3 per cent solution of caustic soda. This is effected in a closed tank, and after a period of about twenty hours the process is completed, when the rubber is removed, washed and dried. This removes the free sulphur, the fabric and many of the fillers like lead compounds and aluminum ones. In 1900, he modified his patent by substituting a rotating cylinder which allowed a better mixing during the treatment with steam.

In 1900, Johan Theilgaard reclaimed waste rubber with the use of potassium cyanide, but this is too dangerous a process to be recommended.

In 1900, Robert Cowan patented a machine for removing foreign matter from old rubber. Before this time, materials like nails, leather, strings and bark had been removed largely by washing. His machine is what is known as a strainer. The rubber is fed into a machine which, by means of double walls, is heated by live steam to a temperature where the rubber begins to soften and then by a worm is forced through the strainer discs which retain the solid particles but allow the passage of the rubber. This machine in some modified form is used today in the reclaiming business in connection with the different processes for removing the iron. Along with it, however, a powerful magnet is also used to remove iron particles. In 1904, L. T. Petersen modified the alkali process by first treating the washed and shredded rubber with the alkali raised only to its boiling point. After the fiber is removed, the rubber is taken from this solution and treated with an aqueous solution of a hydrocarbon or oxy-hydrocarbon such as phenol under high temperature and pressure. The remaining alkali is here combined and the rubber reclaimed or rendered workable.

In 1908, George Capelle reclaimed by using as a solvent the hydrocarbons which result from the distilling of India rubber in vacuo.

In 1909, Auguste Tixier treated rubber waste with terpeneol, which dissolved the rubber, and then he precipitated it by the addition of alcohol.

In 1910, G. S. Heller patented what is termed the Electric Reclaiming Process. The rubber is first reduced to a fine state of division and is then charged into a large metal cylinder which may be stationary and contain agitating paddles on the inside, or it may be a rotating drum thus agitating the solution. Around the container is placed a large band which connects with one of the poles of a generator, and into the center of the drum projects the opposite pole from the generator. The following charge is placed in the retainer: 100 lbs. of ground rubber, 600 lbs. of water, 21 lbs. of sodium hydroxide and 1 lb. of ferric sulphate. The retainer is closed, steam is turned on and the contents heated to from 330 deg. to 370 deg. F., the whole agitated and the electric current will also flow through this electrolyte, thus its name. The process requires from ten to twenty-four hours. The rubber is removed, washed, and dried. In many respects the product resembles that obtained by the alkali process.

David A. Cutler in 1913 recommended the use of zinc chloride as a solvent for the fabric in the place of either acid or alkali. As a workable charge he used: 35 lb. of ground rubber; 87.5 lb. of water; 17.5 oz. of zinc chloride; 4 lb. 6 oz. of oil, which is a distillate from pine wood. This is all thoroughly mixed in a tank and finally heated in a closed vulcanizer at a pressure of 100 lbs. of steam. The rubber is removed and washed.

In 1913, H. W. Kugler modified the alkali process by adding to the charge two to five per cent of aniline. The charge is subjected to a pressure of from 60 to 150 lbs. of steam for eight hours. The rubber is removed, washed and dried.

In 1915, Orrin A. Wheeler patented the following process: "The improved method of treating rubber scrap containing fiber is as follows: The scrap, such as tires, shoes, hose, etc., is ground and pulverized in the usual manner. The pulverized material is then treated with a strong solution (about 20 per cent) of caustic soda and allowed to stand in a cool place approximately from three to five hours. Next the material is placed in a digester which is equipped so that it can be sealed or closed up tightly, and carbon disulfide (CS_2), about one pound more or less according to the character of the material treated to about ten pounds of dry rubber scrap, is added to the material, and then the digester is closed and hermetically sealed. This mixture is permitted to remain in the digester for from one to five hours to permit chemical reaction to occur, the digester being operated during such a period to stir and agitate the mass to facilitate the said reaction and thereby bring about a combination of the sulphur with the cellulose, and so producing a cellulose Xanthogenate. On completion of this reaction, the rubber and fiber are converted into a sticky cohesive mass. Next water in quantity approximately equal to the original dry rubber is added to the material in the digester and the agitation is continued, the water mixing with the cellulose to distend it. Next the mass in the digester is heated by carefully raising the steam pressure in the heating chamber around the digester to approximately 100 lbs., which pressure is kept up for a period ranging approximately from fifteen to twenty hours, according to the stock under treatment, and during such time agitation and stirring of the mass will be continued a part of or all the time. This heating causes the cellulose to become insoluble in water and devulcanizes the rubber in the presence of caustic soda and carbon disulfide. In this process carbon disulfide tends to dissolve the combined sulphur and dissolves all the free sulphur, and when heated produces a high pressure in the digester, thereby causing thorough impregnation of every particle of rubber under treatment and greatly assisting in the recovery of the rubber. The solvent may, of course, be recovered.

In this method of reclaiming rubber, the cotton fiber that is usually destroyed or removed in other processes is permitted to remain with the rubber and utilized and becomes a valuable ingredient in both soft and hard rubber compounds. The rubber and elastic tenacious cellulose unite and intermingle so that an article made therefrom will possess the toughness and wearing qualities of new and pure rubber and will be superior for some purposes, particularly where the article made from the reclaimed product is to be subjected to heat, is exposed to the elements or to the action of oils, acids and alkalis. Since the cellulose of the fibrous material in the scrap is utilized to advantage in the product, the cost is less than under any previous process in which the fiber is destroyed and removed or removed without being destroyed.

An excellent grade of material can be made from the product of the process with the addition of sulphur, and with the addition of some of the cheaper gums, such as pontianiac, acra flake, guayule, an article of a higher grade can be produced at a low cost. If desired new rubber may be added.

A comparatively good grade of reclaimed rubber can be obtained by introducing the alkali and carbon disulfide at the same time, but better results are believed to result from the successive treatment with the alkali and carbon disulfide as herein before set forth.

The invention is not to be understood to be restricted to the precise process and proportions set forth, since these may be modified by those skilled in the art without departing from the spirit and scope of the invention.

In 1916, Gray Staunton ground rubber and cleaned it of fiber by a mechanical process. This material is then mixed in the proportion of 80 per cent waste rubber and 20 per cent dry potassium carbonate. The mixture is placed on trays and placed in a tight heater and steam admitted to a pressure of from 15 to 60 lbs. The sulphur is removed as K_2S_5 which is soluble in water.

Rubber waste may be worked up with linseed oil while heating and the resulting semi-liquid mass treated with sulphur monochloride when a so-called rubber substitute is produced.

In the above we have not mentioned all of the various methods that have been suggested from time to time, in fact very few of the patents have been mentioned, but we have striven to give types. When a careful survey is made of all of these and the many other patents also, it will be perfectly apparent to all that there are only about two methods, namely, the alkali and acid processes, or perhaps a combination of these two into one called the acid-alkali method.

Practically all patents claim to be able to remove all of the sulphur from the rubber, and yet the fact remains that no sulphur-free shoddy is to be obtained on the market. Therefore, there is a limit to the number of times that the same rubber may be put through the reclaimer, and that limit is reached in ebonite or hard rubber. Today hard rubber is generally reduced to a powder and incorporated into compounds simply as an inorganic filler might be. In the mind of the writer the most important thing in the reclaiming business, regardless of the method, is the removing of the fabric and free sulphur at as low a temperature as possible. We know that alkalis have a pronounced accelerating action upon the rate of cure of rubber; therefore, when waste rubber containing free sulphur is placed in a devulcanizer of whatever type, and the alkaline solution added, and the steam turned on until a pressure of 60 lbs. or more is reached, there is every reason to believe that some additional vulcanization is sure to take place although we are carrying on what we term devulcanization.

Then again it is imperative that as much as possible of the alkali be removed from the finished product either by washing or by the addition of a little acid to neutralize it, for if any remains it exists there as an uncontrollable accelerator in whatever compound this shoddy may be used.

By the acid process, the finished product seems to oxidize or deteriorate more rapidly. It becomes hard on the surface and will easily crack.

It might be worth while to try and see what kind of a product could be obtained if the free sulphur was first removed from the ground rubber waste by extraction with hot acetone and then the application of the alkali method. That would prevent any further vulcanization during the reclaiming process.

This question comes as a side issue to that of reclaiming. Is it possible to recover the cellulose in a form or modification from the acid or alkaline solution, depending upon the process used? Great volumes of cellulose are consumed here. Or could the soluble mineral fillers be profitably recovered from these solutions? These questions may be answered some day of course, and make it possible to manufacture valuable by-products from materials that are lost in the methods now used in reclaiming old rubber.

CHAPTER XVII

Preparation of Crude Rubber for Manufacturing

The many processes through which crude rubber must pass before it is turned out into manufactured articles introduce many possibilities of its being ruined, or if not ruined, at least badly injured.

Recall for a moment the steps which we have already mentioned, through which this material has passed; also the different persons who have been directly responsible for its real value. Is it not to be marveled at that we get as good results as we do? The development of plantations under the supervision of trained men has greatly improved the treatment of the rubber in the earlier stages of its manufacture. But even today the native of Africa obtains and prepares his rubber from the vines of that country under very crude conditions; the South American produces better rubber; while the plantation rubber is best of all. The manufacturer of today obtains his rubber supply from all sources, ranging from that produced by the primitive method of the barbarian tinctured with the tricks of fraudulency and deceit which so called civilization has taught him, up to that produced by the more or less scientific method for producing uniform crude rubber.

In this chapter we shall follow the rubber after it arrives at the factory and we see it in the receiving room, on through the processes of

Fig. 33—Up-River Fine Para in Factory Storage

cleansing, drying, milling, calendering, and then leave it ready to be made up into whatever article its particular compound has been designed for.

The Receiving Room

In the receiving room, we find the many varieties of rubber coming from many different sources, from many different species of plants, prepared in many different ways, put up in many different forms and differently stored. All these sorts must be put through the general process and each finds its own proper place in the finished article to which it is best adapted. We shall see therefore all the different shipments each carrying its own number which number identifies the life history of that particular lot. We will find that each lot is kept separate until it has entered into some compound.

At certain times it may become necessary, after receiving large shipments of rubber, to store it for some length of time. This depends a great deal upon the market conditions and also the supply available. When the price is very low, there is a tendency toward large buying which means that it will be stored upon arrival. During certain seasons of the year in normal times, we find more rubber stored than in certain others. But whether stored or taken from the receiving room directly, the first general treatment is the same, namely that of cleansing or washing. The grade of rubber determines how and to what extent this process must be carried out. The time was when all rubber brought into the factory was washed, but today the greater part of the plantation rubber is not washed, that having already been satisfactorily done on the plantation itself. A very small portion of the plantation rubber is washed today in the factory, and only when it is used for certain special articles where the highest degree of cleanliness is required.

Washing

The crude rubbers when taken into the wash room are treated, according to the form in which they come, in different ways. For instance, if the individual pieces are large, they must be cut into smaller ones. The rubber is then soaked in large tanks, which contain warm water, until it is softened. From these tanks, the rubber is taken to a machine known as a

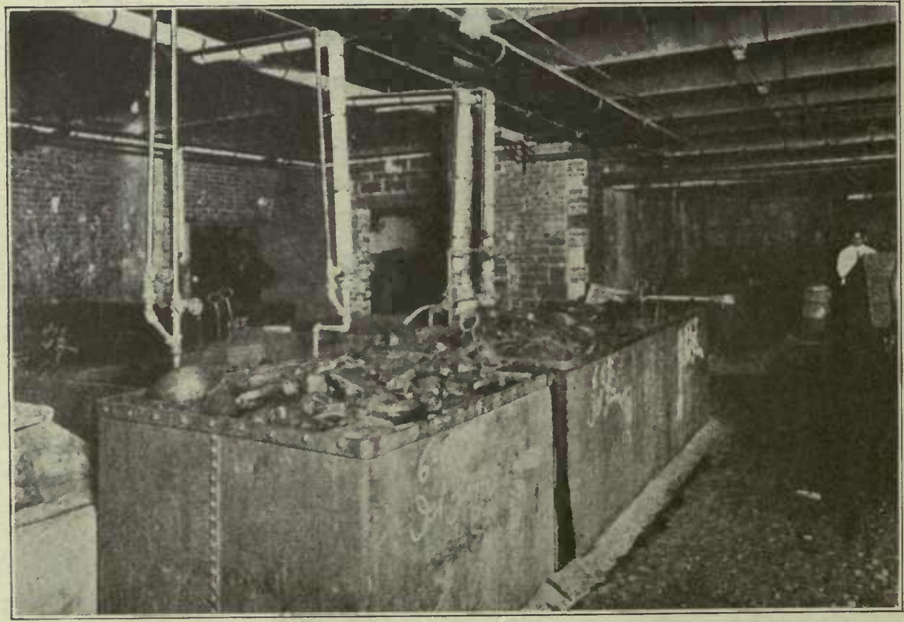


Fig. 34—Soaking Tank

" cracker." This consists of two corrugated rolls turning toward each other at different rates of speed. Over these there is allowed to flow warm or cold water as is desired, while the rubber is passed between the rolls. Here the rubber is first torn into small pieces by means of a more or less grinding action, and for that reason it comes through in a form which is not adherent. In fact it may often be returned through the mill by the use of a shovel. Some kinds of rubber will remain adherent in the form of a thick heavy crepe. Fine Para is of this variety.

In the next step we find a varying practice. In some factories, this rubber, after passing a few times through the cracker, is passed to the adjoining machine called a " washer." It is like a cracker in design but the corrugations of the rolls are much smaller, and the variation in speed of the rolls may not be as great. Here the rubber is washed and assumes a thick crepe form. From here it is given to the third and last machine of similar design with practically smooth rolls, which finishes the washing and leaves it in a thin sheet form.

In some factories the rubber goes through the cracker and is then finished on but one additional machine. That, however, requires the constant changing of the distance between the rolls, and introduces, therefore, the possibility of a variation in thickness in the finished sheets.

Some forms of rubber, after going through the " cracker," are washed in beating machines. These are large oval shaped tanks with a partition running part way through the middle and parallel to their long axis. This partition allows the passage of the charge of the tank past both of its ends. On one side of the tank is placed a rotating cylinder over an elevation in the floor of the tank. When the rubber is placed in this machine and the cylinder rotated, the whole mass will circulate and pass between this drum and the floor thus producing a scrubbing action upon the rubber. This form of washing is used with rubbers which do not adhere well into sheet form.

Special washers have been designed for washing gutta percha and balata. These are washed in hot water in which they become soft. The machines used are automatic to the extent that after the material is added and the machines closed, a kneading process under hot water takes place, and the sand, bark and leaves are re-

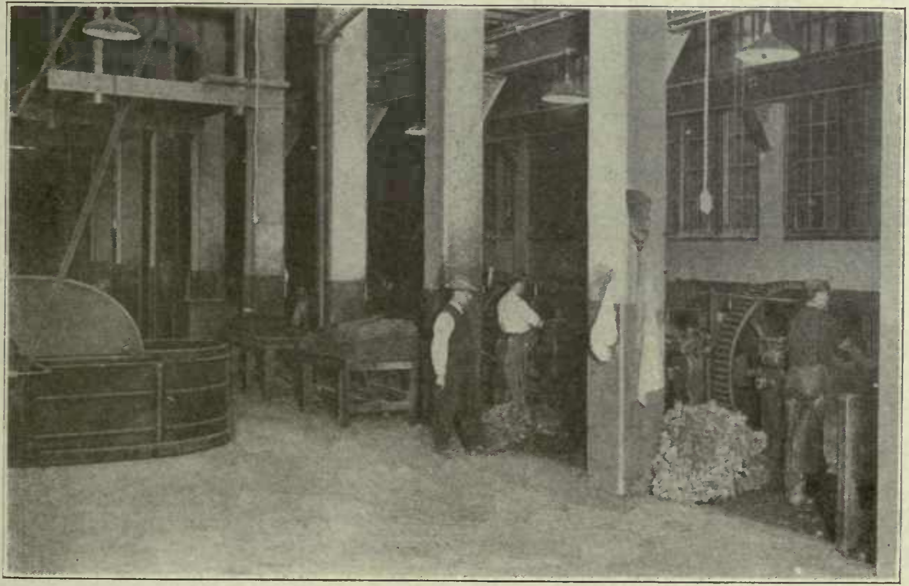


Fig. 35—Washing and Sheeting Rubber

moved. When the resins are removed from this washer they are sheeted in a smooth surfaced mill.

The length of time consumed in washing should be as short as possible. The mechanical working of rubber either on a washer or mill tends to depolymerize it and thus reduces its nerve.

Drying

The next step is the drying of the rubber. This is effected in several different ways. In the early days of the industry, the sheets of rubber were hung in large rooms which were kept rather warm and the rubber gradually dried out. This required perhaps thirty days. The drying room capacity then had to be very large; in fact the minimum would be thirty times the space used each day if it required thirty days to dry out. This process was slow and it required a large amount of space. To hasten this process, therefore, two principles recommended themselves. First, the changing of the air in the drying rooms. As the air becomes saturated with moisture, evaporation takes place very slowly, so by forced ventilation the length of time of drying the rubber was reduced, and therefore the capacity of the drying rooms was increased. Then maintaining these rooms at a uniformly moderate temperature aided materially in the drying process. Where this method is used the rubber is hung over racks. The actual time required to dry the rubber depends also on the thickness of the sheets. As mentioned, it is a big advantage to have the sheets of uniform thickness so that they will all be dried at the same time; this is attained by having the washers set so that the last one through which the rubber passes need not be changed. Some forms of rubber are very soft and in a warm room will so soften that they will not support their own weight when hanging from the racks. To overcome this difficulty a different practice is resorted to.

This consists in removing the water more rapidly from the rubber by placing it in a tight chamber heated with steam coils from which the air may be removed. In other words, the rubber is dried in a partial vacuum. The rubber is placed upon trays which slip into these vacuum driers. Here the rubber is dried in about three hours. This method has received considerable criticism upon the ground that it impairs the nerve of the rubber, and some have contended that it could be used only with certain grades of rubber. But today more rubber is vacuum dried than ever before, indicating that the practice is here to stay.

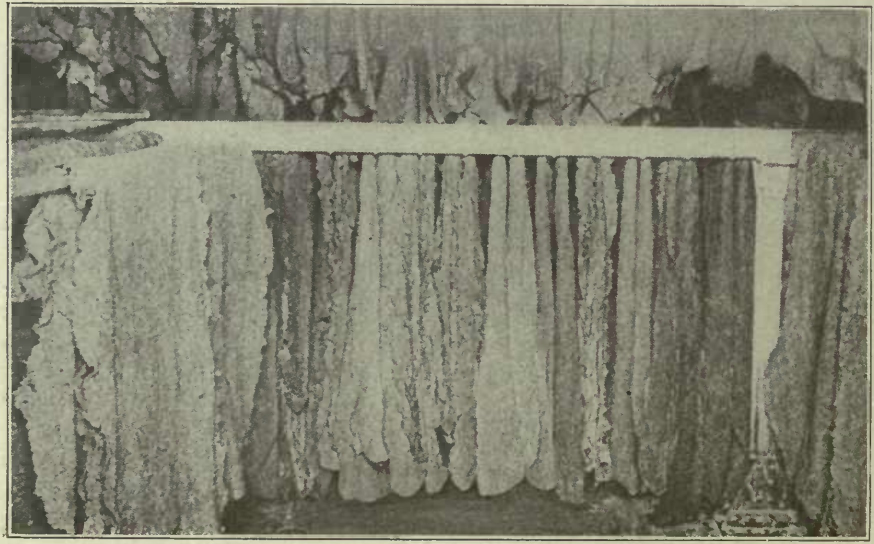


Fig. 36—Stock Drying Room

Another process of drying which has been used in cases of emergency is drying upon the hot rolls of mills. For instance, if the drying capacity of a factory is inadequate to supply the required amount of dry rubber to the compound room, the partially dried sheets are removed from the drying racks and taken into the mill room. Here they are placed upon large hot rolls, the moisture in the rubber is converted into vapor and as such is removed from the rubber. Being an emergency measure, this is resorted to very seldom.

When the rubber hangs in drying rooms, it has been found best to have the rooms darkened as the light seems not only to discolor the rubber but also to break it down or depolymerize it.

From the drying process, the rubber goes to the compound room unless it has been vacuum dried and in that case, it is generally stored for a short time.

Mixing Mills

We shall not discuss the process of compounding here as that will be dealt with in a future chapter, so we next find the rubber weighed out in batches with different fillers ready for the process of milling, or incorporating the fillers into the rubber uniformly. This is done upon mills of varying sizes. The rolls are smooth, and rotate at different rates of speed. Through the axes of these rolls hot and cold water may be circulated either to warm or to cool them as the working of the rubber causes the rolls to become very hot.

The rubber in the batch is first put upon the mill and worked until it is " broken down " or in other words becomes soft and flows evenly over the roll and between the two rolls. When this stage is reached, which is easily observed by the operator, the fillers are gradually added to the rubber and are incorporated into the rubber by returning it through the mill over and over again.

Several things must be observed in milling. As mentioned in connection with washing, the mechanical working of the rubber tends to depolymerize it, and especially is this true where the temperature is above normal. So upon the mill this effect is very marked. Therefore it is desirable to mill the rubber as rapidly

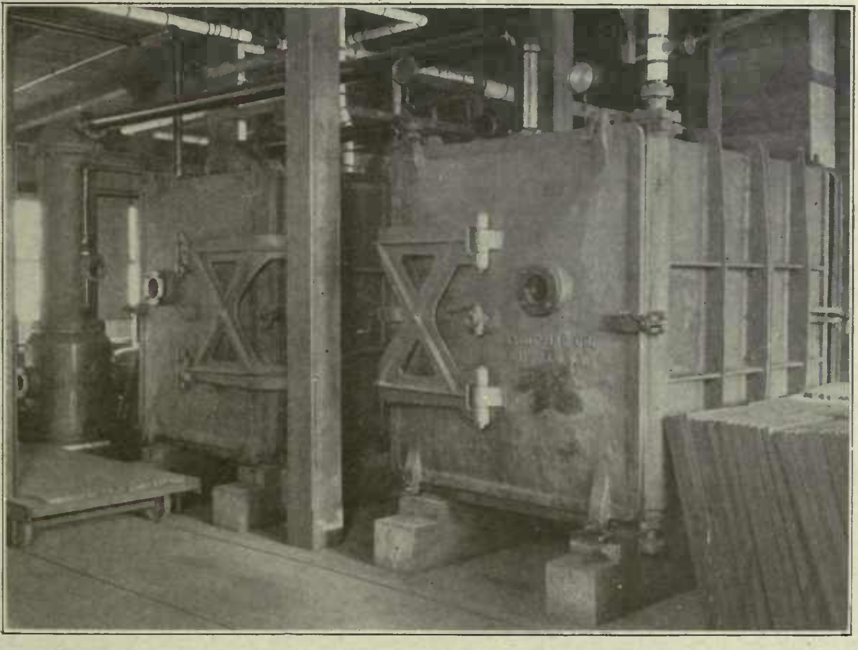


FIG. 37—VACUUM DRYER

as possible and yet it must be worked long enough to make it an even or homogeneous mass. The roll of the mill next to the operator is kept a little warmer than the other and rotates at a slower speed and for these reasons the rubber, while being worked, will remain upon this roll. Here great care must be taken with certain compounds especially, for at the temperature we have here, vulcanization may take place to a certain extent. The temperature of both rolls in a mill is regulated by turning on the hot or cold water and the only way the mill man has of judging the correct temperature is by the sense of touch. " If it feels right " is his only guide. There should be some way of automatically controlling this temperature by means of a thermostat. Some experimental work might be done along this line.

The compounded stocks from the mill room are now allowed to cool to age. Then they are taken to the calender room.

Here the stock is put into a " warming up mill " of the same type as is found in the mill room, the purpose being to soften up the stock again so that it will pass smoothly and evenly through the calender. The calender is used to convert the rubber dough into sheet form of uniform thickness from which the majority of rubber articles are made.

Most calenders are of the three roll type. The rubber coming from the warming up mill is fed between the two upper rolls, passes around the middle one, then between it and the lower roll, and is removed on the opposite side upon a coarse cloth known as a " liner," which prevents the rubber surfaces from adhering together. For sheeting rubber the rolls of the calender are run at equal rates of speed.

Where friction is desired, the calender rolls run at differential speeds. This gives the greatest spreading effect.

The stock, after leaving the calender, is ready to be made up into the articles for which it has been compounded.

To follow the rubber from this point would mean to outline the manufacture of every separate article placed upon the market. We have in this section simply given a general idea as to the handling of rubber in its common processes before it goes into its specialized uses. We have, however, only mentioned the plantation rubber. The great bulk of this rubber without being washed is brought to the compound room, put into batches, and taken directly to the mill room. On account of its previous treatment, it may enter the manufacturing process without being washed and dried in the factory.

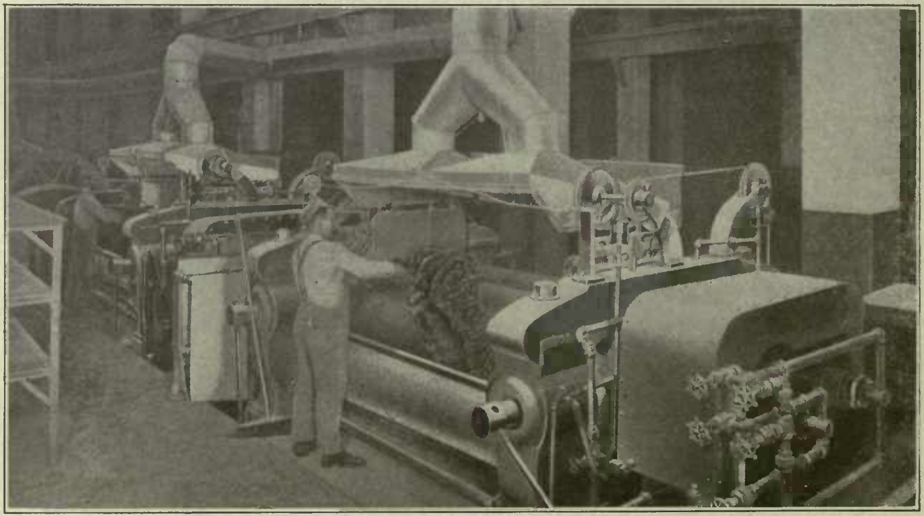


Fig. 38—Close View of Mixing Mills

CHAPTER XVIII

The Principles of Compounding

In this chapter it will be our aim to point out some of the general principles of compounding. Some of these principles are gained from scientific experimenting and some from what is commonly called practical experience. To say that more has been gained through one source than another would hardly seem fair, as each has profited from the other.

The art of compounding, for such it may be called, has developed in the last few years from the point where it was purely a rule of thumb to the extent that today men are trained in the science of compounding. In fact, we may go further and say that the large expenditure of money in the way of equipping laboratories and in hiring men to operate them, is simply for the benefit of the men who are in charge of the compounding. For instance, we may find in a laboratory several men whose whole time is given over to routine work in the testing of crude rubbers, and for what reason? That they may turn over some valuable information to the compounders. We find men, too, testing the purity of the pigments, again to be of assistance to the compounders. Today we find the large laboratories establishing and prosecuting work of a research nature along the line of organic accelerators. This, again, is done with the idea of gaining some knowledge that in the hands of their compounders will enable them to develop greater speed in curing and thus to increase production. The expenditure of large sums annually for research laboratories is justified by the progress made by the companies which maintain such laboratories.

It matters not in what particular line of work the compounding is being done, the same problems are ever before the compounder, whether he is engaged in compounding tires or toy balloons. The following points are all to be considered and each given its due attention:

1—Quality, including tensile strength, elasticity, grain, stretch, set, hardness, resistance to abrasion, to tearing, to cutting, deterioration due to ageing.

2—Adaptability of stock to the processes through which it must pass, such as milling, calendering and spreading.

3—Length of time and conditions required for vulcanization.

4—Compatibility with other stocks with which it is used.

An excellent example of this is found in the different stocks which must be developed in the construction of a solid tire, where it is necessary to produce a stock which will form a union with a metal base on one side and with the soft vulcanized tread on the other:

5—Color.

6—Specific gravity.

7—Cost.

We shall now discuss these points as they bear upon compounding in mechanical goods, dipped goods, tires and hard rubber.

For the compounding of mechanical goods, the problem, with the exception of a few specials, presents itself as follows: The compounder is advised of the terms as called for by the specifications in a contract which includes price, delivery, specific gravity, color, and usually definite tests to which the article must be subjected and pass.

He will, therefore, take the material available and meet the specifications with as much margin of quality as the price will allow. It is to his advantage to make the time of cure as short as possible in order that the equipment may render the maximum possible production. Otherwise the conditions are the same as encountered in other stocks.

We shall therefore take each point separately for discussion.

Tensile Strength

Tensile strength is determined mainly by (a) the quality of the rubber used; (b) the balance between the rubber and other compounding ingredients. This embraces all there is to be said of compounding for in striking this balance, any or all of the properties in (1) are developed. Tensile strength is acquired mainly by the use of zinc oxide and different grades of lampblack. Several other materials effect tensile strength more or less, but these two are in a class by themselves.

Resistance to abrasion, to tearing, to cutting, etc., are very much allied to tensile strength, although the latter is by no means a measure of them. Zinc oxide is, beyond question superior to all other materials for obtaining these qualities, consequently one almost never finds a rubber compound that does not contain zinc.

Grain is another close ally of the properties just mentioned. It is desirable to produce a stock which will have a grain that is more or less knotted up and consequently will prevent easy tearing.

With very few exceptions, the addition of other compounding ingredients to the rubber tend to cut down the strength. In the case of certain materials, such as inner tubes, surgical goods, toy balloons, etc., the stretch is highly desirable and for this reason in their manufacture, very little filler may be used. Such as are used are mainly employed as coloring pigments. In this connection we might mention antimony, iron oxide, arsenic yellow, lampblack, litharge, and various organic pigments.

Occasionally where a cheap stock is desired, barytes may be used as a filler with very little effect upon the stretch; however, in the majority of uses for which a rubber compound is wanted, high stretch is undesirable.

Fig. 39—Stock Bins and Compound Boxes

In tires, for instance, too high a degree of stretch would cause too much flexing resulting in inner friction which would cause the tire to go to pieces in a short time. No rule can be given for a proper balance in regard to this property since it must be worked out by actual experiment in each individual case.

Elasticity

Elasticity is measured inversely by the ratio of the work done in stretching to the work given back by the recovery. It is difficult to prophesy in advance just how a compound will conduct itself in this respect, except that most cheap fillers, like barytes, whiting, etc., have a tendency to decrease this ratio.

" Set " is nothing but an approximate measure of elasticity.

Ageing Qualities

The deterioration of rubber articles upon ageing is undoubtedly one of the most objectionable features. This deterioration may be due to several factors:

(a) Cure, either over vulcanization or under vulcanization.

(b) The quantity of sulphur present, either excess or deficit.

(c) Oxidation, which may be influenced by atmospheric conditions such as heat, light, humidity, alternate wetting and drying, gases in the atmosphere, or in special cases the influence of oils, or other chemicals which may come in contact with the rubber accidentally or of necessity, as in the case where hose is turned to conduct acids or oils. Here special compounding is necessary to produce a more resistant compound.

By adaptability to working on the mill or calender, we mean that the compound must not be too soft, neither must it be too dry. In certain cases precaution must be taken to produce stock that will not scorch too readily. Again, in the case of frictions, it is necessary to produce the desired degree of tackiness for frictioning. In the tubing machine, some stocks may be too dry and thus come through rough; some may swell unevenly after coming through the die of the tubing machine. Some stocks will give trouble due to blooming when being calendered. This will cause poor unions in case it is used in laminated fabrications. Thus if the stock is soft, either add some filler or remove some of the softeners. If too dry the reverse of this will undoubtedly prove the remedy. Mineral rubber, vaseline, pitches, tar and cheap wild rubbers, and vegetable oils may be used for these purposes.

In a large number of cases it is necessary to cure two or more stocks of different nature together. The cure of each of these stocks must be regulated so that both will be cured properly during the same length of time. We will take, for example, solid tire stocks. Here the volume of rubber is so great that there is a tendency for the outside to cure more rapidly than the inner part unless the time of vulcanization is long enough to permit the whole mass to acquire the same temperature and remain at this temperature long enough so that the time to heat through and to cool off in the center will approximately balance. Then, again, where tires are vulcanized by the two-cure process, the carcass gets a fair degree of cure in the first heat but must retain the property of holding its shape and at the same time that of uniting with the tread rubber during the second cure. The tread rubber on the other hand must take a " set " cure very quickly and be able to hold its shape and form a union with that already in the carcass. These properties may be obtained by proper manipulation of the sulphur content and by the use of suitable accelerators.

Colors

The next point is that of color. Here the compounder is asked either to duplicate a certain stock as to color or to produce a stock of certain color. This is a point which is most important in mechanical goods. Of course, the trade may become prejudiced in favor of a certain color in treads or a certain color of inner tubes, but the choice is limited to a very few shades, while in the case of balloons, variety of tints is to be desired. The number of colors available when only inorganic fillers were used restricted the selection very much, but today with the use of organic dyes many different shades and tints are possible. When compounding to match a certain shade, one often encounters difficulty for it cannot always be foretold just what effect the process of vulcanization is going to have upon the particular color pigments which are added, and especially is this true of certain organic ones.

Specific Gravity

Very often the compounder is asked to produce a stock of a certain specific gravity. This is done by having at hand a knowledge of the specific gravities of the different materials used in compounding. In this connection we will give an example. For instance, it is desired to produce a stock having a specific gravity of 1.59. Let us assume that the purpose for which this stock is to be used will allow the compounder to use fine Para, zinc oxide and sulphur. This is a very simple formula but the principle may the better be grasped from it. The compounder arranges his data in the following manner:

Material	Weight	Specific Gravity	Volume	Cost	Cost of Weight
Fine para	50	.89	56.1	$.81	$40.50
Zinc oxide	x = (54.9)	5.35	$\frac{x}{5.35}$	.10	5.49
Sulphur	3	1.98	1.51	.04	.12
	107.9				$46.11

Conclusion

From his experience he concludes that he will use 50 parts of rubber with a specific gravity of .89, and to cure this three parts of sulphur with a gravity of 1.98. The question that remains is to determine the amount of zinc oxide necessary to give the stock a gravity of 1.59. In other words, the amount of zinc oxide is an unknown quantity, but has a gravity of 5.35.

Now the volume $= \frac{\text{Wt.}}{\text{Sp. gr.}}$ therefore, the volume of rubber is equal to $\frac{50}{.89} = 56.1$. The volume of zinc oxide is equal to $\frac{x}{5.35}$ and the volume of sulphur is equal to $\frac{3}{1.98} = 1.51$. Now the total weight of the compound as taken is $50 + x + 3 = 53 + x$ and its volume $56.1 + \frac{x}{5.35} + 1.51 = 57.61 + \frac{x}{5.35}$, and since Vol. $= \frac{\text{Wt.}}{\text{Sp. gr.}}$ ∴ Sp. gr. $= \frac{\text{Wt.}}{\text{Vol.}}$. Wt. $= 53 + x$; Volume $= 57.61. + \frac{x}{5.35}$

Thus 1.59 (the desired gravity) $= \frac{53 + x}{57.61 + \frac{x}{5.35}}$

Therefore x = 54.9 parts of zinc oxide necessary to fulfill the above conditions.

Volume Cost

From the same problem we may illustrate what is meant by volume cost in compounding. Filling in the costs and quantity of zinc oxide in our data we find that 107.9 pounds of this stock will cost today $46.11, therefore, the cost of one pound will be $.427. This stock has a gravity of 1.59, therefore, a cubic foot of it will weigh 62.4 (a cubic foot of water) times 1.59 or 99.216 pounds. We have already determined the cost per pound to be $.427, therefore, the cost of a cubic foot or volume cost, as it is termed, will be $.427 times 99.216 or $42.36.

From the above example the method of compounding with reference to cost will also be illustrated. If the volume cost must be necessarily low, then cheap rubber and pigments must be used. If on the other hand, quality is not to be sacrificed for cost, then better materials may be employed. In this connection, however, a compounder is able to save large sums of money for his company, where he is able to produce a quality equal to or better than their competitors at a lower volume cost. Experience here is a valuable asset. A wide experience and knowledge of fillers and rubbers, with a clear understanding as to what may be accomplished with each one, constitutes the requisite for a good compounder. Let us point out just a few of the many troubles that must be guarded against. First, some dirt may get into the compound, either through the fillers in their handling, or in the rubber itself, and as a result many dollars' worth of goods may be lost. This is especially true in the case of compounds which contain a high rubber content, like tubes or band stock. The rubber will not adhere to the dirt particles during vulcanization, and when finished and the rubber is stretched it separates from the foreign body and this leaves a hole and weakens the goods at this point.

Second, moisture to any extent in any of the materials used in a stock is very objectionable. If moisture is present when the stock goes into the vulcanizers and is heated above the boiling point of water, this enclosed moisture will exist in the gaseous condition and cause " blowing " or the making of the stock porous. Again, it may come out toward the surface and there cause " blistering "; again, it may discolor white stocks, and, again, if present in fabric, it will cause poor unions in tire construction.

Third, if the fillers contain any lead compounds or the batch pans from a previous stock, and these happen to find their way into what is supposed to be a white compound, they will discolor it.

Fourth, great care must be exercised and close vigilance kept of what is going on in the compounding room. Should the wrong kind or the wrong amount of material be used or a certain material be left out of a compound, it will be liable to throw that stock out in cure, color and gravity, thus rendering it unfit for the purpose for which it was to be used.

Scorching

Fifth, scorching on the mixing mills, calender or tube machines is usually due to forcing the stock to run faster than it should, too high temperature, too much speed or insufficient warming up. Quick curing stocks especially suffer from these causes. The best way to get them plastic so that they will run through other processes more easily, is to work thoroughly on the mixing mills before any powders are added, or, in other words, be sure the rubber is well broken down.

Sixth, what is termed " tough stock " is generally caused from insufficient milling of the rubber before adding the fillers. Then, too, some compounds have a tendency to toughen on long standing. Some stocks may come off from the mill in good condition, but before the heat, caused in mixing, has had time to radiate out, the rubber will be piled in bins, thus trapping the heat, and there will take place a certain degree of vulcanization. The result is similar to tough stock, but is really a scorched condition.

Seventh, a lumpy stock may be produced in several ways. For instance, the presence of dirt, as mentioned above, may cause it; or lumps which occur in shoddy which has not been evenly reclaimed or refined; then, too, the mixing of tough stock or scorched stock with a soft compound may be responsible.

Eighth, sulphur bloom on uncured stock, such as friction and cover stock, may be due to using tough or scorched stock, insufficiently "warmed up " stock, too high a temperature on the calender, and, under some conditions, too low a temperature.

Ninth, poor union of stocks may be due to some incompatibility of the stocks to be joined, improper preparations of stock in mill rooms, dirt, moisture, soapstone, or anything which may affect the tacky surface of the rubber, incompletely dried cement, or poor local workmanship.

Tenth, porosity of the cured stock may be due to moisture as mentioned above, insufficient pressure, under cure, or improper compounding.

Eleventh, surface pitting is closely related to porosity or blowing, and is caused by air trapping, surface moisture, or perhaps the same causes which produce porosity.

Twelfth, improper cure is a thing which must be closely watched. If a sample is over-cured it cannot be brought back, for the process of vulcanization is not reversible, as pointed out when we discussed reclaiming. Over-cured stock may or may not lack in tensile strength, but it always lacks in stretch, is always short grain and ages very poorly. On the other hand, under cure lacks in tensile strength, resiliency and generally in aging properties. Therefore, the vulcanizing must be closely checked.

Thirteenth, as mentioned above, it is difficult to match certain shades of color due to variations of materials used.

CHAPTER XIX

Chemical Analysis of Manufactured Rubber

In this chapter we shall aim to outline only methods which may be of some practical use to men in the laboratories. We shall not attempt to go into the subject to the extent of the complete analysis of a sample of rubber, but shall sketch methods for the determination of facts which the man in charge of the laboratory is anxious to have in the way of control work.

The first thing necessary is to obtain a fair sample of whatever material is to be examined. What was said in a previous article dealing with the chemical analysis of crude rubber in regard to the obtaining of a sample applies here as well. Very often the stock furnished is composed of but one mix and in such cases it is a fairly easy task to obtain a uniform sample. However, when the sample submitted is composed of several different mixes and these have been vulcanized, thus forming a compact mass, the problem is a more difficult one. As an example of the former instance, we have such stocks as inner tubes which are very easily sampled; while as an example of the latter, we have the casing of an auto tire. Here we have a certain mix for the bead, another for the friction, another for the sidewall, another for the tread, and still another for the cushion or breaker. In the latter case, the chemist must take a knife and scissors and proceed to dissect the sample, taking out the different portions which represent different mixes. It takes some time and experience to obtain good samples of the friction especially.

Procedure of Analysis

We shall now outline the general procedure of analysis, assuming that the sampling has been carefully done.

It is never necessary to analyze manufactured rubber for moisture.

The analysis may be divided into two parts, both of which may be run by the chemist at the same time, the one dealing with the organic materials present and the other with the inorganic.

Determination of Organic Content

For the examination of the organic content, we take advantage of the action of different solvents thus removing certain materials by extraction methods.

To allow the use of such practice the sample must first be reduced to a finely divided state so that the solvent exercises its maximum effect. This is accomplished either by running the sample through a digester, if it is of a nature to allow this treatment, or, as in the case of ebonite, it may be filed; but very often it is necessary simply to cut the sample into as small pieces as possible with the scissors.

The first solvent which is employed in determining the organic portion is acetone. The acetone used for this purpose should be colorless, and if it has colored upon standing it should be redistilled over potassium carbonate before being used.

A weighed sample of the finely divided rubber is placed in an extraction thimble of the desired type. We prefer a Bailey-Walker which is provided with a Wiley block tin condenser. The thimble is then placed in position and the rubber extracted with hot acetone for a period of ten hours. Some have contended that ten hours is not a sufficient length of time, and, of course, it is not for ebonite, but for the vast majority of cases it is perfectly safe and where exceptions come the analyst must use his own judgment as to the proper length of time. During the extraction the operator should note frequently the general appearance of the extract. If the extract slowly turns yellow and has a slight fluorescence it indicates the presence of bitumens, while if it is strongly fluorescent, it indicates coal-tar pitch. Mineral oil manifests itself here also by making the extract fluorescent yet it does not color it to any extent.

When the extraction is completed, the extract is allowed to cool and carefully observed, for some materials are soluble in hot acetone but crystallize out on cooling. This is true of paraffin. The separation of oily drops generally indicates factice. The extract is now evaporated over a water bath to dryness in a weighed container. Here is the advantage of the extraction apparatus mentioned above —the flask is of such size and shape that it can be weighed and the extract evaporated to dryness in it, while if a Soxhlet apparatus has been used it is customary to transfer the extract to a smaller tared dish for evaporating. This introduces the possibility of loss and also the waste of acetone in washing while transferring from one flask to another.

When evaporating to dryness, if there is very much free sulphur present, toward the end of the process there is liable to take place very violent pounding and thus the loss of some of the residue on account of its being spurted out. This may be overcome to some extent by the addition of a little benzene when the evaporation will continue quietly to dryness. When the evaporation is complete the flask is dried in an oven. Some chemists have recommended that the flask be dried in a hot air oven for an hour at 110 deg. C. while others claim that it is better to dry for three hours at 60 deg. C. The latter is the practice in this laboratory, for we have found that some of the rubber resins are volatile at 110 deg. C. When dried this is weighed and thus the total acetone extract is determined which in itself is of little value. In this residue is to be found the free sulphur, resins, oils either mineral or fatty, and paraffin. In addition to these there will be the acetone soluble part of the factice, or reclaim, or bitumens and pitches which might have been used in the rubber stock.

Determination of Sulphur

The first component in the acetone extract to be determined is sulphur. Many methods have been suggested and much discussion has been given to this particular subject. However, from a practical standpoint, the following method or methods give accurate enough results for control work at least.

The weighed residue in the flask in which we carried out the extraction, is covered with dilute nitric acid (1-1) and a cover glass placed over the mouth of the flask, while it is warmed over a water bath. Care must be taken here that the reaction is not too violent, for if such should happen, some of the sulphur might be lost. After the first reaction is over about 5 c.c. of a saturated solution of potassium chlorate is added and the solution allowed to heat over the water bath until the sulphur and the organic matter has all disappeared. In some places the potassium chlorate is added in the crystalline form, but it is our experience that it is much more effective as an oxidizing agent here if it is first dissolved and its solution is added. The length of time required for the complete oxidation varies a great deal and the only safe procedure is to judge from the appearance of the flask. In same cases additional nitric acid must be added and this may be the concentrated. In some instances where oxidation seems to be very difficult, we often make additions of fuming nitric acid. This will generally complete the oxidation in a short time. The solution is then evaporated to dryness over a water bath, or to a syrup if that is as far as it will go. There is no danger of losing any of the sulphur by the volitization of the sulphuric acid over a water bath, as the sulphur now exists largely as the sulphate of potassium due to the fact that potassium chlorate has been added. The residue is now taken up in water to which a little hydrochloric acid has been added, and if a clear solution does not result it is filtered while cold. The filtrate is then brought up to boiling and before adding the barium chloride, which is the customary procedure, we are indebted to A. C. Carlton for a slight modification which we have found to work beautifully and which causes the barium sulphate to settle very rapidly in a granular form which will allow of its filtration in thirty minutes' time.

Barium Sulphate Troubles

If to the hot filtrate containing the sulphate you add 10 c.c. of a saturated water solution of picric acid and then the barium chloride drop at a time, then allow it to stand until it has settled your troubles with barium sulphate will be eliminated. The picric acid washes out from the barium sulphate very easily. The sulphur is then determined in the usual manner, by burning off the carbon of the filter and igniting until white. The sulphur is obtained by multiplying the weight of the barium sulphate by 0.1373.

We have oxidized the sulphur in the acetone extract by the use of nitric acid and bromine and obtained very good results. It has been claimed that in order to oxidize all the free sulphur, in the presence of these organic substances, in addition to its nitric acid treatment the residue left upon evaporation should be fused with a mixture of five parts of anhydrous sodium carbonate and three parts of potassium nitrate. For work of a research nature this might be necessary, but not for the work in a commercial laboratory.

Some volumetric methods have been suggested but we shall not take the space here to outline these but refer to the Thiocyanite method of C. Davis and J. L. Foucar, *Jour Soc. Chem. Ind.* 31 (1912), p. 100.

Determination of Mineral Oil, Vaseline and Paraffin

The estimation of mineral oil, vaseline and paraffin is not carried out quantitatively very often. As stated above the appearance of the acetone extract furnishes a clue as to their presence and in actual work a man's knowledge of the stock gives an idea as to the amount of these materials which might be used. Where it is desired to make their determination, it is necessary to extract a new sample with acetone and to use the extract for the determination. The method consists in destroying all the other substances in the extract except the paraffin compounds by the use of concentrated sulphuric acid. To accomplish this, 2 c.c. of concentrated sulphuric acid are added to the extract in the extraction flask, covered with a watch glass and heated in an oven for from three to four hours at a temperature of 110 deg. C. The contents of the flask are then extracted with petroleum ether several times and the washings transferred to a tared flask after having been shaken up in a separating funnel with a soda solution containing some alcohol. The petroleum spirit is then evaporated off and the flask is dried in an oven for two to three hours at 110 deg. C., then weighed and its percent determined.

The other components in the acetone extract are difficult of determination and really do not add very much to the knowledge of the sample under consideration.

Some chemists have led us to think that by a determination of the rubber resins in the acetone extract it is possible to say what variety of crude rubber is used in the stock. This may be true in a certain few cases where the resins have a peculiar odor which identifies them, but it is not general enough to be dependable.

The next general procedure is to gain some idea as to the amount of bitumens and pitches. The appearance of the acetone extract, as already stated, gives us a qualitative test as to whether or not these substances are present; but if there is a question as to their actual existence in the sample, the following test may be applied:

Either some of the fresh sample or some of the acetone extracted is placed in a test tube and covered over with carbon disulphide, and if either bitumens or pitches are present, they will be dissolved and color the solution; then by use of pyridine as a solvent you may distinguish between the two as it is a solvent for the pitches but not for bitumens.

If either of these are found to be present the residue left in the thimble from the acetone extraction is dried by allowing it to remain out in the air when the acetone will soon evaporate, then placed in an extraction apparatus and extracted for several hours with carbon disulphide; four hours is generally sufficient. The extract is then distilled and the residue dried in an oven three hours at 110 deg. C. and the weight of the residue determined. This will not represent all of the bitumens or pitches as part appeared in the acetone extract; in fact this extraction will contain from ten to thirty per cent of the total amount in the original stock. It is plain therefore that this determination is of value only to the extent of giving us a general idea as to the amount of these substances present. Here again a man's judgment and experience must fill in the rest.

Determination of Rubber Substitute

The last experiment, which is made upon the sample for its organic content, is to ascertain a knowledge of the factice or rubber substitute present.

To carry out this advantage is taken of the behavior of these substances with alkalies. Under the chapter dealing with rubber substitutes, we pointed out the fact that these materials were saponifiable.

To carry out this test successfully the rubber must be in a very finely divided state for the penetrating power of the alcoholic potash solution is very small.

The residue left in the thimble from the carbon disulphide extraction is dried and in some cases may be reduced to a fine powder. It is then transferred to a flask, preferably one which has a ground glass connection with a reflux condenser. Then there is poured over the rubber the alcoholic solution of potash. Some laboratories use a N/5 solution, others N/1, and some N/2 solution. The more concentrated the solution, the smaller the amount needed. The rubber is now boiled in this solution over a water bath for about three hours when all of the substitutes should have saponified and colored the solution to some extent, depending of course as to whether brown or white factice has been used. From this point two procedures have been used and are in use in some places today, although the one is subject to grave criticism.

We shall outline the better method first. In this the solution is poured off from the rubber into a flask and the rubber is then washed three or four times by boiling it up with 20 c.c. of water, each portion being added to the flask in which the original solution is contained. The combined solutions are then evaporated over a water bath to a volume of about ten or fifteen cubic centimeters. This clear solution which contains the soap from the saponification of the substitutes is then transferred to a separatory funnel, and when cold acidified with either hydrochloric or sulphuric acid when the corresponding fatty acids will be liberated from the soap. These are extracted with ether three or four times and the ethereal solution evaporated in a tared flask, and dried at 110 deg. C. for an hour. The weight and thus the percent of factice removed by this treatment is then determined, but it must be remembered that part of the factice was removed by the acetone extract; also that we are weighing here the organic acid and not the factice itself, therefore a correction must be made. To apply this correction, it must be determined whether white or brown factice was used and to ascertain this a test is made for chlorine in the alcoholic potash extract. If it is present, white factice was used; otherwise it was the brown substitute. To correct, therefore, for the white factice, the amount of organic acid is multiplied by 1.136, and if chlorine is absent, thus indicating the brown, multiply by 1.064. This final amount of factice also falls short of the amount actually used in the compound by the amount that was dissolved by the acetone extract. So by experiment it is necessary to make another correction and if brown substitute was used the amount found is increased by one-fourth, and needless to say this same amount should be subtracted from the acetone extract. If white factice was used, then an addition of one-ninth is necessary.

The alternate method for factice determination consists in thoroughly drying the residue in the thimble left after the carbon bisulphide and weighing it. Then subject it to the same alcoholic potash treatment as mentioned above in exactly the same manner. After effecting the saponification, the rubber is filtered on a tared paper, washed with boiling water several times before being transferred to the filter, then dried and weighed. Its loss in weight is taken as being the saponifiable part and thus calculated as factice. This method leads to poor results, due to the fact that it is very difficult to wash out of the rubber the last traces of the alkali, but worse than this, we know that many fillers are soluble in strong alkali and parts of these will be removed and thus be calculated as substitutes. Such fillers as lead, antimony and zinc all behave in this manner.

There are certain instances where it is suspected that both white and brown substitutes have been used in the compound. To determine this fact a new alcoholic extraction must be made and the extract is then evaporated to dryness; 1 c.c. of water is added and then more heat is applied when the majority of the organic matter will be destroyed. By the use of a spatula, sodium peroxide is gradually added with continued heating until the whole melts. The mass is then allowed to cool and is taken up in water and made up to a definite volume. This is divided and in one portion chlorine is determined and in the other sulphur. For the chlorine determination, the solution is acidified with nitric acid and the chlorine precipitated and determined by the addition of silver nitrate.

The other portion is acidified with hydrochloric acid and the sulphur estimated by the addition of barium chloride in the manner outlined above. The percentages of sulphur and chlorine in white substitute do not vary much so that it is safe to calculate for the amount of chlorine present the corresponding amount of sulphur and the excess sulphur present is a measure of the amount of brown substitute used in the compound.

Determination of Rubber Content

This finishes the analysis of any sample for its organic content with the exception of the caoutchouc hydrocarbon itself. Considerable work has been done with the idea of finding some method by means of which the rubber proper might be determined, but at present none of the methods suggested allow of its accurate determination.

The general practice is therefore to arrive at the rubber content by difference. This method is subject to criticism if the inorganic matter present is determined by ashing the sample, for during this treatment some of the components are changed chemically and some may even be volatilized.

But now we are able to determine the inorganic matter by the use of solvents whereby the rubber is dissolved and washed away from the pigments with the aid of centrifugal machines.

The true rubber content is then arrived at by adding together the percentage of the various extracts, the sulphur added for vulcanization and the inorganic matter and subtracting this total from 100. This method has the disadvantage that it places all the errors in the previous work upon the rubber content, and yet it gives results accurate enough for commercial work. In some cases the caoutchouc may be determined by the tetrabromide method as modified by Spence. But too many other factors come in to cause trouble for it to be regarded as a reliable method.

The nitrosite method proposed by Harries and Alexander is too long and too tedious a method to recommend itself, especially when the results are somewhat questionable.

Having dealt in the last section with the organic portion in a sample of manufactured rubber, we shall now proceed with the inorganic part.

Determination of Sulphur

The first component to be considered is sulphur and it bears a very important part. We have pointed out the determination of the free sulphur as it was found in the acetone extract but in manufactured rubber we must also know the amount of combined sulphur. By this we mean the amount of sulphur in combination with the caoutchouc itself, for in addition to this we have sulphur in combination in the fillers used, as in the case of antimony, which is really only present in the form of the sulphides of antimony, and in the case of lead sulphide which is formed during vulcanization when litharge is used in the compound, in lithopone, as sulphur in zinc sulphide, and also here as the sulphate of barium. Sublimed lead also has sulphur in the form of lead sulphate. Then again we have the sulphur which exists in factice or rubber substitutes, and a little in mineral rubbers. These represent some of the places in which we may expect to find sulphur.

With these facts in mind we proceed to determine the coefficient of vulcanization or degree of vulcanization. To obtain this knowledge, we must determine the total combined sulphur in the sample which we will represent by x; the total sulphur which is in combination with inorganic substances which we will designate as y; then the expression $(x\text{-}y)$ will equal the amount of sulphur in combination with the rubber proper.

The formula then which represents the degree of vulcanization is represented thus $V = \frac{100\,(x\text{-}y)}{z}$ where $V =$ degree of vulcanization, $z =$ amount of caoutchouc, which is generally determined by difference. This as was pointed out before is liable to an error of several per cent.

To determine the x, or the totally combined sulphur, it is necessary to use a sample which has been subjected to all of the extractions, the acetone removing the free sulphur, the carbon bisulphide removing a small amount of sulphur as it occurs in the mineral rubbers, and the alcoholic potash removing the sulphur found in factice.

For this assay many methods have been suggested but we shall outline only a few of these.

First a weighed amount of the rubber is placed on the crucible and covered with a watch glass and some concentrated nitric acid is added. When the violent reaction is over the watch glass is removed, and the solution is evaporated to dryness over water bath. In case there are some rubber particles still remaining, the nitric acid treatment is repeated. To the contents of the crucible a fusion mixture of sodium carbonate and potassium nitrate is added and when thoroughly mixed is covered and very gradually heated. When the reaction takes place it gives off a considerable amount of energy and therefore the reaction may be rather violent. When this is over the temperature is raised and the whole mass brought to a quiet fusion and held there until it appears homogeneous. In some cases the fusion is poured out on an iron plate and when cold is lixiviated with water along with what remains on the crucible. It will be necessary to filter this solution for it will have suspended in it the carbonates of the different metallic fillers used. The filtrate is acidified with hydrochloric acid and evaporated to dryness, taken up with a little hydrochloric acid and water and again filtered if necessary. The sulphate is then determined as outlined before.

In this test as in all others, blank tests should be run with the chemicals to make sure they are all free from sulphur.

Another method which does not take a long time and gives good results is the following:

About fifteen grams of potassium hydroxide are placed in an iron or nickel dish with two c.c. of water and heated until it is dissolved, then a weighed amount of rubber which has been extracted is added and the heating is continued. Smoke will be given off and there will be a little sputtering which always comes when the mass is being stirred. The mass turns black, due to the charring of the rubber and now sodium peroxide is added in small portions until the whole mass comes into a quiet state of fusion and the carbon disappears. The contents of the dish are allowed to cool and then taken up in water and acidified with concentrated hydrochloric acid until the iron oxide, which comes from the action of the fusion upon the dish, has dissolved. If there remains a white precipitate it is probably barium sulphate and it may be filtered off and weighed thus getting the sulphur in it. The filtrate is treated for sulphur in the usual manner; then the two are added together. Very often when barium sulphate is precipitated in the presence of iron salts there results considerable adsorption of the iron with the result that when the barium sulphate is ignited it is colored yellow or even reddish brown. In such a case the contents of the crucible are dissolved in concentrated sulphuric acid, with the aid of heat if necessary, and then the solution is poured into a beaker of water when the barium sulphate will reprecipitate, is filtered out and ignited again when it will be white.

The methods mentioned under free sulphur have been used here also—namely oxidizing with concentrated nitric acid aided either by potassium chlorate or bromine. But these methods are not applicable if an insoluble sulphate like barium is present. These are the methods used most frequently.

The y in the above formula or the combined inorganic sulphur is determined as follows: A weighed amount of the residue obtained by dissolving away the rubber from the charge, as will be outlined below, is placed in an iron dish with about five grams of potassium hydroxide and then boiled down and oxidized with sodium peroxide as outlined above. The mass is dissolved in water, acidified with hydrochloric acid and the process is continued as outlined above. This will give the sulphur inorganically combined which taken from the totally combined sulphur gives the amount in union with the caoutchouc which multiplied by 100 and divided by the amount of caoutchouc gives the degree of vulcanization.

Analysis of Mineral Matter

For the analysis of the mineral matter which was put into the compound the old incineration method is unreliable.

The best method today consists in placing from 0.5 to 1.0 gram of the rubber in a weighed centrifuge tube about five inches long and an inch in diameter. The rubber is then treated with from 10 to 15 c.c. of a distillate obtained from petroleum having a boiling point around 200 deg. C. or a little higher. The tube is fitted with an air condenser about two feet long and then heated in a paraffin bath so that the solvent just boils.

The length of time necessary to disintegrate the rubber varies considerably. Where the degree of vulcanization is low a few minutes will be sufficient, but, as the degree of vulcanization goes higher, the time required to effect solution is longer. As the rubber approaches ebonite, this method becomes impossible.

When the solution is complete it is allowed to cool, when the mineral matter will settle and the supernatant liquid is decanted. The mineral residue is then washed with light petroleum spirit and the tube placed in a centrifugal machine and centrifuged until the supernatant liquid is free from solid particles. In the majority of cases this requires from twenty to thirty minutes, and at the end of this time the mineral matter is a hard compact mass which allows the liquid to be poured or siphoned off without loss of residue. This washing is repeated several times and each time the residue must be broken up with a spatula to enable effective washing. The residue is then dried to constant weight and the per cent of mineral charge thus ascertained.

The reason that we use the centrifuge tubes from the beginning is that it saves transferring the solution which gives considerable chance for error.

From this point on we proceed almost as though we were carrying out an inorganic analysis. First, however, we must carefully inspect the mineral charge, for there may be in it fiber, lamp black, etc., and these along with other materials may be identified by an examination with a magnifying glass. Also before taking portions for analysis the whole residue must be carefully ground and mixed because the process of centrifuging has divided it into a more or less stratified condition, the heaviest fillers being thrown out first and the lightest ones last.

A weighed portion of the residue is now placed in a beaker or evaporating dish and treated with dilute hydrochloric acid. Note whether any CO_2 or H_2S is given off. The solution is evaporated to dryness over a water bath and the residue moistened with concentrated hydrochloric acid, again evaporated to dryness and then heated in an oven at 110 deg. C. for one hour. Moisten the residue again with hydrochloric acid, then add 200 c.c. of water and bring to boiling, then filter on a tared paper. If there is a large amount of lead present, it may be necessary to boil up the residue with more distilled water, filter and combine the filtrates. The residue is dried and weighed. It may contain barium sulphate, silica, carbon, and organic matter. The residue is then ignited and weighed. In the majority of cases, this ignition loss is a fairly good indication as to the amount of carbon present unless the silica runs high, as determined later, in which case part of the loss is due to water.

The residue is now placed in a platinum dish, if it was not ignited in one, moistened with hydrofluoric acid and a drop of sulphuric acid added, then evaporated to dryness over a water bath, ignited and weighed. The loss in weight here, of course, represents the silica, and the residue the barium sulphate. In some cases this residue is colored reddish brown due to the presence of iron which may be eliminated as pointed out above. Sometimes the residue is fused with an alkaline fusion mixture and then analyzed in the usual manner. Thus the barytes and siliceous materials are determined.

The filtrate from the acid-insoluble is acidified with hydrochloric acid and, as far as rubber fillers are concerned, when hydrogen sulphide is conducted into this solution we expect to see either a black sulphide of lead form, or an orange one of antimony. Our idea as to which one is pretty well fixed also for if the original sample was gray or black we expect lead, while we expect to see the antimony if the stock was red. Of course there are times when the above reasoning does not hold.

The hydrogen sulphide precipitate is dissolved in nitric acid, then a little sulphuric acid is added and the solution evaporated until fumes of sulphuric acid appear. The solution is then cooled, 75 c.c. of water and 25 c.c. of alcohol added, and allowed to stand an hour when the lead sulphate may be filtered off, washed with water containing alcohol, ignited and weighed as lead sulphate.

Some volumetric methods for determination of lead may also be used.

The antimony sulphide is washed into a weighed crucible and nitric acid added, then evaporated to dryness over a water bath. Fuming nitric acid is then added, evaporated again, then gently heated and finally ignited and weighed as SbO_2.

If other sulphides beside antimony are thrown out of the acid solution by hydrogen sulphide, they may be separated by the use of sodium sulphide.

The filtrate from the sulphides which is acid with hydrochloric acid and also contains some hydrosulphuric acid, which during the hydrogen sulphide precipitation has reduced the iron, if any is present, to the ferrous state, is boiled to remove the hydrogen sulphide and nitric acid is added to oxidize the iron. During this boiling there will be a separation of sulphur which must be filtered out. Some ammonium chloride is then added and the hot solution made alkaline with ammonium hydroxide. The precipitate which forms is composed of either the hydroxide of iron or that of aluminum, or perhaps both. A good idea of this is judged from its color.

The solution is filtered. The residue is ignited and weighed as Al_2O_3 or Fe_2O_3. When it is necessary to actually determine the amount of iron and aluminum, that is done in the usual manner by dissolving out the Al_2O_3 with sodium hydroxide. The filtrate from the iron group is made alkaline with ammonium hydroxide and the zinc precipitated as sulphide. The sulphide of zinc is very difficult to filter, but if the ammoniacal solution is warmed and hydrogen sulphide conducted into it, it comes down in a form which filters comparatively easy for zinc. After the zinc sulphide is filtered out and washed it is dissolved off the filter paper with hydrochloric acid into a weighed crucible. The solution is then evaporated over a water bath, freshly precipitated mercuric oxide is added, carefully heated and ignited to constant weight, thus giving the amount of zinc oxide.

The zinc is easily determined volumetrically by dissolving the zinc sulphide in dilute hydrochloric acid and titrating it with a solution of potassium ferrocyanide, which has been standardized against a known zinc chloride solution, using uranyl nitrate as an external indicator. This gives very good results.

The calcium in the filtrate from the zinc is determined by adding ammonium oxalate to the hot solution. The calcium oxalate is filtered off, washed, ignited to constant weight and determined as calcium oxide. The magnesium left after removing the calcium is precipitated in the cold solution by adding disodium hydrogen phosphate and proceeding in the usual manner.

Determination of Carbon or Graphite

It is weighed as $Mg_2P_2O_7$ and then calculated to MgO. This constitutes the general procedure of analysis of a sample of manufactured rubber.

As amorphous carbon and graphite are used in large quantities their determination is sometimes required.

One or two grams of the original rubber is placed in an evaporating dish and covered with nitric acid, the dish being covered with a watch glass until the first reaction is over, then the solution is evaporated to dryness over a water bath. If any rubber remains the process is repeated. When the rubber has all disappeared, the residue is washed into a large beaker and boiled up with 400 c.c. of water. The solution is then filtered through a tared filter, washed several times with hot water, then transferred to a beaker and boiled up with dilute ammonium hydroxide to which a small amount of ammonium chloride is added. The solution is again filtered through the original tared filter paper and washed with water. The residue is again transferred to a beaker and this time boiled up with dilute hydrochloric acid, filtered upon the tared filter, washed, dried and weighed.

This residue may contain mineral matter which was insoluble in nitric acid, ammonium hydroxide and hydrochloric acid. For instance, barytes and silica will both withstand this treatment. So the residue is now ignited and the carbon burnt off. The weight of the residue taken from the weight left in the tared filter will give a very close approximation to the true amount of carbon used. The carbon in the residue may be determined accurately by placing the dried carbon residue in a combustion furnace and running a regular carbon combustion. This is seldom if ever necessary.

CHAPTER XX

Physical Testing of Compounded Samples

In addition to the chemical analysis it is necessary to make a number of physical tests of compounded samples.

It is obvious in the beginning that not all the physical tests known should be carried out on every sample submitted. For example, it is hardly necessary to test a solid tire for elasticity nor submit a toy balloon to an abrasion test.

We shall discuss the following tests and the reader will be able to judge where each will be used to advantage:

1. Tensile strength
2. Elongation
3. Set
4. Hardness
5. Rebound
6. Hysteresis
7. Abrasion
8. Penetration
9. Tearing
10. Specific Gravity
11. Ageing Tests
    a. to heat
    b. to light
    c. to weather
    d. to artificial conditions
12. Dielectric Power
13. Viscosity
14. Special Tests for pneumatic tires
    a. Friction test
    b. Wearing tests on test cars
    c. Test tires
15. Special tests for solid tires
    a. Barbeque test
    b. Road tests

No single one of the above tests is sufficient to recommend or to condemn a sample, but several that are applicable must be tried and as a result of all these one arrives at a conclusion.

Practically all of the above tests are to be carried out in a laboratory and therefore they are all more or less artificial. By this we mean that we are not subjecting the sample to the actual conditions under which the rubber will be used but we try to approach these conditions and from the results obtained speculate as to how that rubber will conduct itself under the conditions for which it was designed.

Of course the most valuable test to which we can put any compound is to try it out where it is to be actually used, but such tests consume too much time before results are available. Then again the compounder wants to try out many new compounds, designing them for special purposes, and if it is possible to gain the information from some simple physical tests in the laboratory it saves both time and money. With this understanding we shall discuss the above physical tests.

Tensile Strength

The first in order is tensile strength and here we find several conditions which influence the results obtained. For instance, the kind of machine used; the shape of the test pieces and how they are made; the speed at which the load is applied; the temperature of the rubber when the test is being made; and the grain of the rubber.

There are several machines on the market each possessing certain merits. The ones in common use are the Scott, Olsen, Cooey, Schopper and Schwartz. Due to certain differences in these machines, and the peculiarities of rubber, it is difficult to obtain results which check well by using two different makes of machines. The

Cooey runs a little more rapidly than the Olsen, and, as a matter of fact, the Cooey machine will show a greater tensile than the Olsen. Therefore it is necessary when striving to obtain some comparative tests to use the same machine, whatever one that may be.

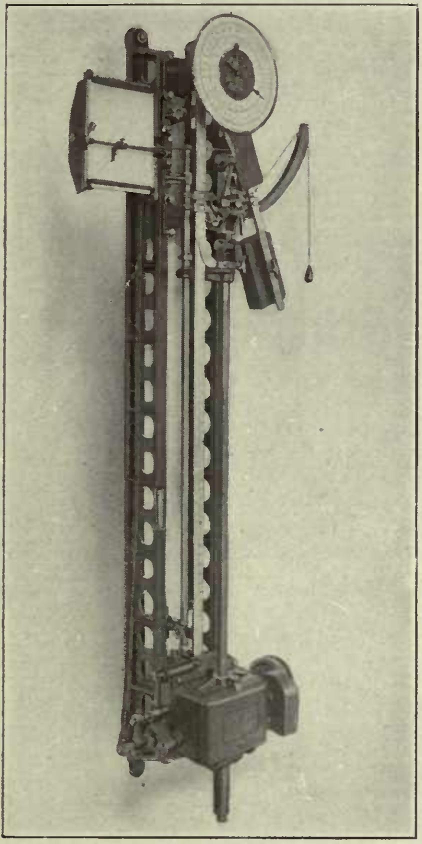


Fig. 40—A Scott Rubber Tester

The shape of the test piece and the way in which it is made is an important point in connection with tensile tests.

The two forms most in use today are the straight pieces, which are enlarged at each end to allow the fixing of the clamps, and the ring form. The American machines use largely the straight pieces while the Schopper machine uses the ring form. These test strips are made either by cutting them out of a cured sheet by means of a die either with a press or by striking with a mallet. In some cases the sample is cured in a mold of the desired form for the test piece. This latter method is not as satisfactory as the use of a die, for if there remains a rind on the test piece after being removed from the mold, it must be trimmed off, and, in so doing, it is a very difficult matter to avoid nicking the test piece itself; and if that is done the sample will fall short of its correct tensile strength due to the tearing which will start from that point.

In using the die, care must be taken to keep the cutting edges sharp and free from nicks. It will also be found that dipping it first into a basin containing a little water, just to moisten the cutting edges, will greatly aid in the work.

In connection with the Schopper machine, there is a die press for cutting out the rings and also a caliper for determining the thickness of the sample. It is difficult to obtain the true thickness of the sample unless it is made from stock which has been calendered before curing, for otherwise it will vary some. The width is governed by the die and is generally one-quarter of an inch as shown by the accompanying Fig. 41.

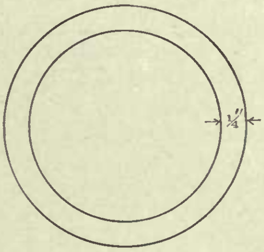


Fig. 41

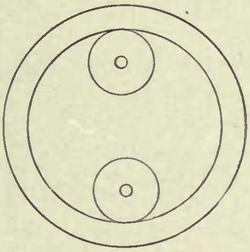


Fig. 42

Fig. 43

Fig. 42 illustrates the ring test placed over the two pulleys of the Schopper machine ready to be tested. Fig. 43 represents the same ring after the test is begun and the pulleys have moved apart a short distance and it will be observed that in such a test piece, the outer circumference of the ring is stretched more than the inner circumference, or in other words it is under a greater strain than the inner and consequently the ring will fall short of its true tensile due to tearing. This is the greatest objection to the ring form.

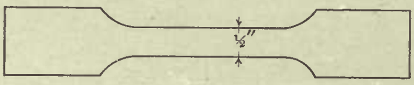


Fig. 44

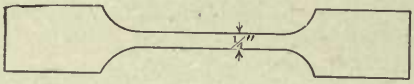


Fig. 45

Fig. 46

The accompanying figures will illustrate the straight test pieces. Fig. 44 is termed the short one-half inch strip and is used with very elastic stocks which will not break in the range of the machine. Fig. 45 is the one-fourth inch die and is used with stocks which have a high tensile. Fig. 46 is a short one-fourth inch die and is used with stocks possessing both a high tensile and a great elasticity. Ordinarily a test piece fails at its narrowest point and thus effects the break inside of the marks on the rubber. In ordinary work it has been stated by the Bureau of Standards that the small test pieces will give larger values than the larger strips, and in this connection the following data has been obtained.

Die Used.	Tensile.	% Elongation.
D ½ in.	2440	470
E ¼ in.	2845	612
F ¼ in.	2538	575

From these figures the truth of that claim seems to be confirmed.

Fig. 47

To study the problem still further, sixty-four stocks were prepared and from each of these one ¼-inch die, Fig. 45, was cut and one ½-inch, Fig. 44, was taken. Then each strip was tested in the same machine. There were forty-nine instances where the ½-inch gave a tensile of 100 pounds or more greater than the ¼-inch piece, thirty-three cases where the ¼-inch piece proved that much the better, and forty-six cases where the two checked within 100 pounds. From this work it would seem that the differences in actual results are slight, whether the large or small strip is used. Considerable has been said concerning the speed with which the load is applied during a test. It has been known for some time that this point has a definite influence upon the tensile strength of a stock. That is the tensile strength indicated in a test depends to some extent upon the speed with which the rubber is stretched.

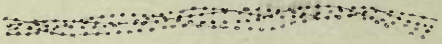


Fig. 48

And in Bulletin No. 38 of the Bureau of Standards the results of their experiments illustrate that point very clearly:

No. 1			
Speed in in. per min.	5	25	45
Tensile strength per sq. in.	2495	2690	2720
Elongation %	605	635	635
No. 2			
Speed in in. per min.	5	25	45
Tensile	1900	1940	1970
Elongation	465	500	400
No. 3			
Speed in in.	5	25	45
Tensile	375	430	465
Elongation	340	360	375

From these figures, it is apparent that as the speed with which the load is applied is increased, the tensile strength will be higher. Of course there is a limit to this where increasing the speed will have no further effect upon the results.

The average speed adopted for machines today is from twenty to twenty-four inches per minute and this constant speed will always give comparative results, and that is what is desired. However, if check work is being done and different machines being used it would be advisable to take this factor into consideration.

The temperature of the rubber when the test is being made also influences the results. Here again the Bureau of Standards has given some valuable experiments. Four stocks were made up and then test pieces taken, which were later tested at 50° F., 70° F. and 90° F. Before each test was made, the room in which the work was done was maintained at the temperature desired for at least three hours. The exact results of these tests may be found in the Bulletin 38 referred to above.

First they found that the variation between 50° and 70° was much greater than between 70° and 90°, and as a result the Bureau now carries out these tests at 75° F. This is a temperature fortunately that is fairly easily maintained in working conditions.

"Grain"

When a sample of rubber is milled and perhaps calendered all in the same direction there results what may be termed "grain." Then if this sample is cured, the one cutting the test pieces has the choice of cutting them parallel with this grain or transverse to it. From considerable work done along this line it is plainly evident that the direction in which the sample piece is cut does influence the results, therefore when obtaining comparison upon stocks, care must be taken in this particular. A theory by way of explanation of the phenomenon has been suggested by a friend and Fig. 47 illustrates the arrangement of rubber particles in a crude sample of rubber. The particles may be considered as chains linked together as colloidal aggregates by fine threads similar to those obtained when a stirring rod is dipped into a glue gel and then is removed. As a result of the treatment through which the rubber has passed these chains are extending in all directions. Now during the milling there is a tendency to straighten out these chains and thus bring them closer together as shown by Fig. 48.

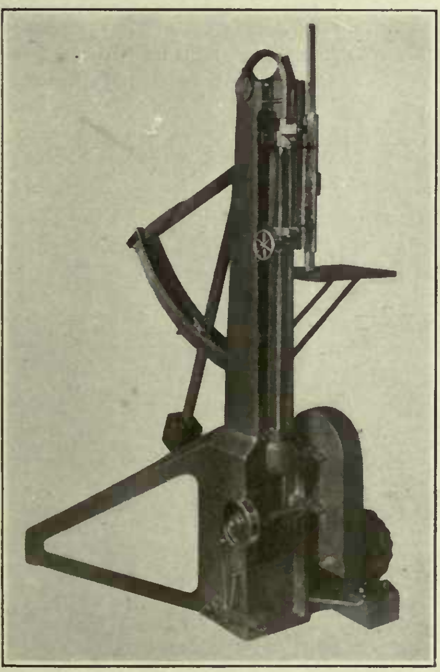


FIG. 49—OLSEN VERTICAL TESTING MACHINE

If the above theory has anything of truth in it, we should expect that a test strip cut longitudinally should contain more of the chains and thus give a larger tensile test than a strip cut transversely or across the grain.

To test this point the Bureau of Standards prepared four samples, taking both longitudinal and transverse test strips from each, and obtained the following results:

Tensile strength	1	2	3	4
Longitudinal	2730	2070	1200	880
Transverse	2575	2030	1260	690
% Elongation—				
Longitudinal	630	640	480	315
Transverse	640	670	555	315
Permanent Set after 300% elongation for one minute with one minute rest.				
Longitudinal	11.2%	6%	22.1%	34.3
Transverse	7.3	5	16.3	25.0

From these figures we see that the tensile strength is greater in the longitudinal one, as would be expected. The permanent set runs higher in the longitudinal one also.

Therefore we must take into consideration the above facts when carrying out tensile strength determinations.

In addition to these points, a great deal of care and trouble is caused by the jaws which grip the test strips.

As the rubber stretches its cross section grows less, therefore a jaw must be used which will tighten as the load is applied.

The ring form of course obviates

these troubles for the rings pull around pulleys.

One of the best forms of jaws is that used by the Olsen machine where eccentric disks grip the rubber and pull tighter as the rubber elongates.

The weight shown by the machine should be indicated by a lever arm and not by a spring, as the latter requires calibrating too often.

The actual determination of the tensile strength is then accomplished by pulling such a test strip whose exact thickness and width is known in one of the machines used above and then calculating and reporting the number of pounds which it requires to break a strip possessing a cross sectional area of one square inch.

For example a test strip having a thickness of 11/64 of an inch and a width of ½ inch, sustained a pull of 180 pounds before it failed. Its tensile strength is figured thus:

½ times 11/64 = 11/128 square inches cross section area and this pulled 180 pounds, therefore its tensile strength will equal 1/11 of 180 = 16.4 times 128 = 2029 pounds. The elongation test is generally carried out at the same time as the tensile strength test and on the same machine.

On the test piece, a distance of two inches is carefully marked off before placing it in the machine. As the load is applied, the distance between the two marks is carefully measured and when the sample fails the distance is recorded in inches. The elongation is then figured as the per cent the original two inches is of the length it stretched before rupture. As an example the sample above elongated 11.3 inches, therefore its elongation is 11.3/2 times 100 = 565%. The ring form machines are the only ones that possess an automatic device for recording the elongation and such an improvement will be welcomed for the other machines.

The "set" or recovery is also determined at the same time as the above. The method used extensively has been to place the broken ends of the test strip together and measure the distance between the two marks which originally bound the two-inch distance before breaking. The measurement is made one minute after breaking and is referred to as immediate set in contrast to permanent set which is the more valuable. The set is also calculated in percent and represents the ratio of the stretch of the two inches to the total elongation.

From the above example the two-inch marks were found to be 2.6 inches apart after rupture and the elongation was 11.3 inches, therefore the immediate set is equal to $\genfrac{}{}{0pt}{}{11.3}{2.6 - 2}$

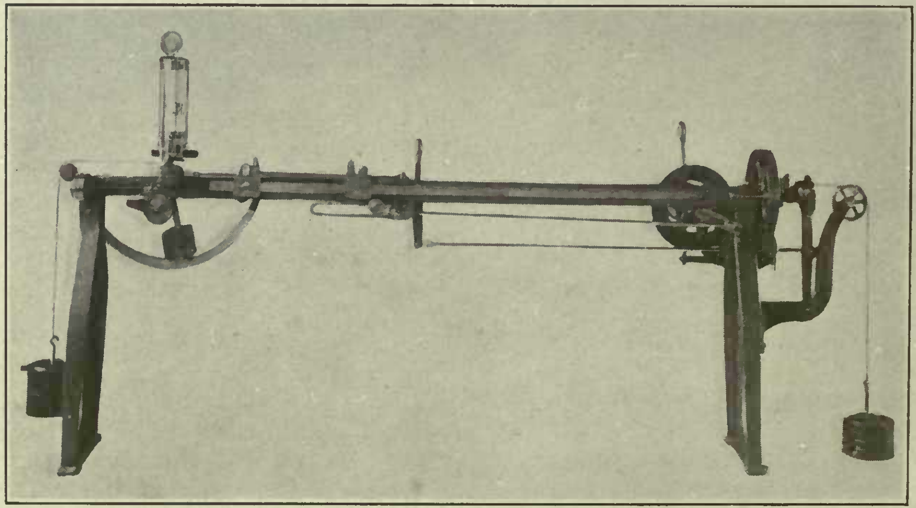


Fig. 50—Olsen's Autographic Rubber Testing Machine

times 100 or 5.3%. Several methods have been tried and recommended for ascertaining permanent set. Beadle and Stevens suggest that the sample be stretched 400% and be held for twenty-four hours, then released and measured six hours later. This will give comparable results if adhered to for general work, but requires too much time.

In this as in immediate set there is the probability that in many specimens this will not give the true recovery for there is likely to take place a tearing or breaking down of the rubber and this of course decreases the set. Along this line the following experiment was tried:

Half inch test pieces were prepared and then stretched 75% of the breaking elongation. That is, if a sample elongated 13 inches it was stretched 9.75 inches and held for one hour, two hours, three hours, eight hours, and sixteen hours. The set was measured then in one minute, ten minutes, twenty minutes, forty minutes and sixty minutes and showed the following:

Time extended.	1M.	10M.	20M.	40M.	60M.
1 hr..........	.65	.49	.49	.46	.46
2 hr..........	.65	.63	.60	.50	.45
3 hr..........	.65	.55	.53	.52	.50
8 hr..........	.68	.56	.54	.53	.52
16 hr..........	.75	.70	.67	.60	.53

As a result of this experiment, the following method which is easily and rapidly carried out is to be recommended:

The sample is stretched 60% of its elongation and held five minutes, then released and allowed to rest for three minutes. The sample is subjected to this stress three times, then allowed to rest ten minutes and measurement made. By this shorter method about 98% of the permanent set is found.

Hardness

Next in order of the physical tests is the property of "Hardness." This is a property very difficult to define, which is possessed by all samples of rubber from the softest vulcanized rubber on one hand to the hardest vulcanite on the other. Various instruments have been manufactured and sold for the purpose of determining this property and yet no entirely satisfactory instrument is to be had at the present time. The general plan upon which these instruments have been constructed consists of a plunger of some sort with a point varying from a blunt needle up to a foot of quite measurable area. The measurement is taken of the depth this plunger will sink into the sample under a definite given load: Or what amounts to the same thing the measurement of the force necessary to cause the point of the plunger to sink into the rubber a definite depth. Under all circumstances such an instrument should have a point sufficiently blunt that the surface of the sample shall not be ruptured during the test.

These tests are the measure of the penetration by a blunt point without rupture of the rubber. The "rebound" may be considered a test for resiliency.

The instrument for this purpose consists of a metal tube with a slot along one side which is graduated from zero at the bottom to 100 at the top. A ball is placed in this tube in such a way that it may be allowed to fall freely through the tube its graduated height when in a vertical position. The tube is put in place over the sample of rubber, which must be resting upon a firm base, in such a position that with the ball resting free on the sample it levels at zero on the scale. The ball is then raised until it occupies the same position with reference to the 100 mark. It is then released and the distance it rebounds is carefully noted. This test is repeated as many times as seems desirable preferably at several different points on the sample, then the average of these results is taken.

This test is especially valuable on stocks used for cushioning.

Hysteresis

One phase of rubber testing which has received but comparatively little attention and that quite spasmodic, is the so called hysteresis test which really has to do with the contour of the curves representing the relation of the stress to elongation under the conditions of extension and recovery on not only the first but also on repeated extensions. This includes:

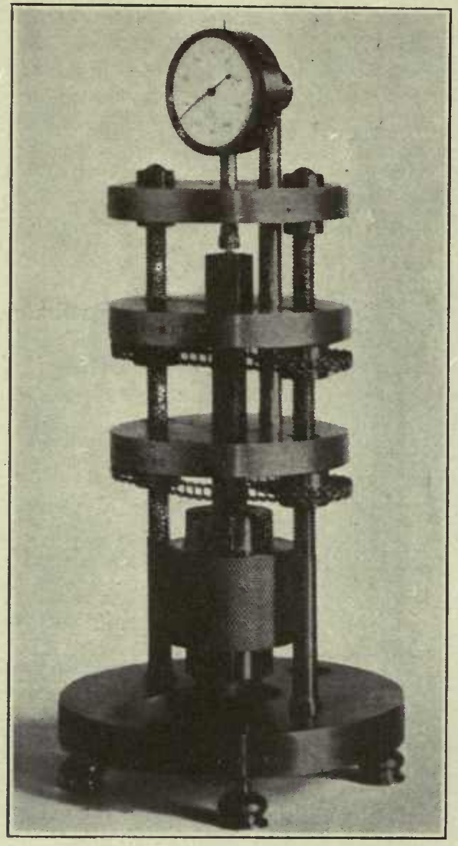


FIG. 51—A PLASTOMETER

1—The detail of the contour of the respective curve.

2—The area under each respective curve which in turn represents the work required for extension, and the work done by the sample in retracting, the difference representing the work lost or hysteresis loss.

3—The relation of the contours and areas represented by these different curves to each other. This of course includes the relation between the percentage of elongation produced by the same load under repeated flexing as well as the relation of the loads required to produce the same elongation. It also takes in the increase in set under repeated flexing.

The reason for the lack of progress in this promising field becomes quite evident after an inspection of the necessary prerequisite of test specimens. These may be enumerated as follows:

1—The piece must be longitudinal and of uniform cross section throughout the entire length on which the graph is being recorded.

2—The several pieces which are being compared should be of the same cross section because of the difficulties in correcting for each of the infinite number of individual points on the curve for the difference thus produced and the resulting difference in the area produced underneath.

3—No portion of that section of the piece on which the record is being made can be subjected to the action of the jaws of the testing machine because of the numerous variations produced by cutting, tearing, slipping, etc.

4—Pieces with enlarged ends are entirely out of the question because of the great difference in percentage of ultimate elongation produced in various increments of the length of the piece under any increment of load. These differences are so great as to completely obliterate those characteristics which are most sought.

5—Ring-shaped pieces are open to the same objection because of the great difference between the length represented by the inner and outer circumferences.

The difference in cross section between two pieces of the same shape may be either corrected, or, in case the cross sectional area is sufficiently large, the difference may become so small as to be negligible.

Two methods of getting around the other difficulties have been suggested to the writer. The one is to follow two marks made on the narrow part of an ordinary longitudinal test piece with trammel points which are so connected with the recording device that only the actual increase in distance between the points is recorded. This device is a feature of the Tinius Olsen rubber testing machine. It is, however, practically impossible to produce a smooth curve with this device. The other method is to attach clips similarly rigged, at the two marks on the piece. This scheme offers a chance for good development.

Assuming that these points have been satisfactorily met, let us proceed to discuss the results to be obtained.

Many men make much use of the relative general contour of the curves produced in the ordinary manner by the usual testing machines. They find themselves able to check their ideas on cure, stiffness, etc., with much greater precision. Some make a practice of accurately comparing several points on the curves. It would therefore seem highly desirable to have an equation for the entire curve in which the various constants would present a ready and accurate means for such a comparison.

M. Cheneveau and Heim have attempted such an equation (*Sur l'extensibilité du caoutchouc vulcanisé Compt. rend. p.* 320, *Feb.* 6. 1911, and in *The Rubber Industry* reports of the London convention in 1911). M. Cheneveau in *Le Caoutchouc et la Gutta percha* has later retracted his belief that the equation holds. E. L. Davies published a short article (*Jour. Ind. to Eng. Chem. VI.*, 985, 1914), with confirming experiments. In his lectures at the Municipal University of Akron, Mr. Davies has explained some further work along this line as follows:

The equation does not seem to hold on the return curve or on the curve for successive cycles nor has he been able generally to apply the methods for obtaining the constants as explained by Cheneveau and Heim. A much more simple and accurate method is presented through resorting to the principles of calculus. Fig. 52 represents the ordinary type of curve:

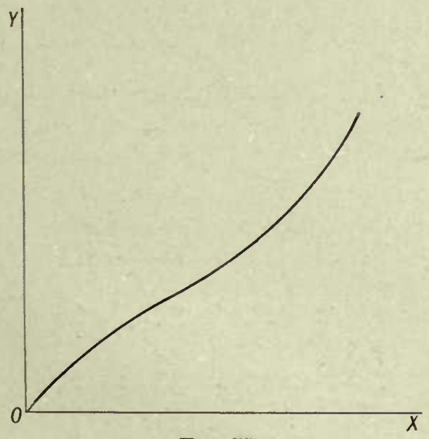


FIG. 52

Assume that this curve is represented by the Cheneveau and Heim equation:

(1) $$x = ey + a \sin^2 by$$

$$\frac{dx}{dy} = e + 2ab \sin by \cos by$$

(2) $$= e + ab \sin 2by$$

$$d^2 x = 2ab \cos 2by$$

Now if we remember that

(4) $$\frac{dy}{dx} = \frac{1}{e + ab \sin 2\,by} = \text{the slope}$$

of the tangent at any point we may draw the tangent and at any point find its slope and substitute in this equation.

Then again bearing in mind that the second derivative is equal to zero at the point of inflexion, if we are able to estimate this point with fair accuracy to be at the point represented by $x'\ y'$, we have

(5) $$\text{Cos } 2by' = 0$$

(6) or $$2by' = \frac{\pi}{2}$$

whence $$b = \frac{\pi}{4y'} = \frac{45^\circ}{y'}$$

and from (4) since at $y = 0$ or at $y = 2y'$, $\sin 2\,by = 0$ we have

$$\frac{dy}{dx} = \frac{1}{e} = \text{slope of the tangent at}$$

either of these points (this gives another proof of the correctness of taking e as the inverse of the tangent at the origin as suggested by Cheneveau and Heim).

Again at the point of inflexion sin $2\ by' = 1$ whence (8) $\frac{dy}{dx} = \frac{1}{e + a\,b}$ = slope of the tangent at the point of inflection and from (1) and (6)

$$x' = ey' + a \sin^2 \frac{\pi}{4}$$

$$= ey' + \frac{a}{2}\left(2 \sin^2 \frac{\pi}{4}\right)$$

$$= ey' + \frac{a}{2}\left(1 - \cos\frac{\pi}{2}\right)$$

$$= ey' + \frac{a}{2}$$

wherefore

$$(9) \qquad a = 2\,(x' - ey')$$

We do not need any of this proof for a working basis, but have simply to remember that having located the point of inflection at x' y' we can draw the tangent at either the origin (where the curve is apt to be irregular and therefore not ordinarily to be chosen) at the point of inflexion, or at the point where the ordinate of the point of inflexion and having drawn it determine its slope. The constants are then found from the following simple equations:

$$a = 2\,(x' - ey')$$

$$b = \frac{\pi}{4y'} \text{ or } \frac{45^\circ}{y'}$$

e = the inverse of the slope of the tangent at the origin or at the point where the ordinate is twice the ordinate of the point of inflexion.

Or e may be determined by equating $\frac{1}{e + ab}$ to the slope of the inflexinal tangent.

If we wish to find the area under the curve up to any point represented by $x_p\,y_p$ we may integrate this equation as follows:

$$\text{Area O, } (x_p\,y_p),\ x_p,\ \text{O} = \int_{y_0}^{y_p} ey\,dy + \int_{y_0}^{y_p} a\sin^2 by\,dy$$

$$= \frac{ey_p^2}{2} + \frac{ay_p}{2} - \frac{\sin 2by_p}{4b}$$

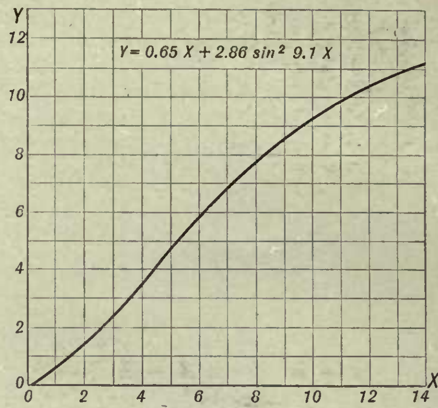


FIG. 53

The chart here reproduced was drawn by means of clips attached at marks 2 in. apart on a test piece measuring 0.5 in. by 0.125 in. It was drawn on cross section paper ruled 20 lines to the inch. Because the recording device reversed the curve on the chart, the equation becomes

$$y = cx + a\sin^2 bx$$

The unit of ordinate 0.5 in. represents 34 per cent elongation; the unit of abscissa represents 167.5 lb. per sq. in. stress. One square inch therefore represents 22.32 ft. lb. of work done.

By taking the point of inflexion at $x_1 = 4.95$ and $y_1 = 4.65$ and using the foregoing equations.

$a = 2.86$

$b = 9.10 \text{ deg.} = 0.18 \text{ radians.}$

$c = 0.65$

and the equation $y = cx + a\sin^2 bx$ becomes

$$y = 0.654x + 2.86\sin^2 9.1x$$

Comparing with actual figures we get

In considering these results, it must be remembered that 0.05 in. on the chart represents 16.75 lb. on the x

	X	Y computed.		Y actual.		Diff. (%).	
Abs.	lbs. per sq. in.	Ord.	% Elong.	Ord.	% Elong.	Elong.	Error.
1 = 0.5″	167.5	0.72	24.6	0.63	21.6	3.0	14.5
2	335.0	1.58	54.0	1.45	49.6	4.4	11.2
3	502.5	2.55	87.2	2.47	84.5	2.7	3.1
4	670.0	3.61	123.0	3.55	121.5	1.5	2.4
5	837.5	4.71	161.0	4.70	160.5	0.5	0.3
6	1005.0	5.80	193.0	5.80	198.0	0.0	0.0
7	1172.0	6.85	234.0	6.78	232.0	2.0	1.2
8	1340.0	7.82	267.0	7.68	263.0	4.0	1.5
9	1507.5	8.66	296.0	8.55	293.0	3.0	1.3
10	1675.0	9.36	320.0	9.25	316.0	4.0	1.3
11	1840.0	9.92	339.0	9.85	337.0	2.0	0.6
12	2010.0	10.25	351.0	10.35	353.0	2.0	0.6
12.75	2135.0	11.85	405.0	11.70	400.0	5.0	1.2

axis or 3.4 per cent elongation; the maximum difference shown was, therefore, only about the width of the mark made by the tracing pen, and that the recording device was very crude.

Integrating.

$$y = 0.65x + 2.86 \sin^2 9.1x$$

$$da = 0.65 \int_0^{12.75} x\,dx + 2.86$$

$$\int_0^{12.75} \sin^2 9.1\, x\,dx$$

$$\text{Area} = \left[\frac{0.65x^2}{2} + \frac{2.86x}{2} - \frac{2.86 \sin 18.2x}{4 \times .18} \right]_0^{12.75}$$

$$= 69.06$$

$$= \frac{69.06}{4} = 17.26 \text{ sq. in.}$$

The area obtained by means of the planimeter on this area is not available to the writer at present, but the two results differed by less than 0.1 sq. in.

The various relations between the areas of the various loops made by the initial and successive extensions and retractions should give a great deal of very desirable information especially with regard to the resiliency of the stock and the rate of diminution of the same.

Beadle and Stevens have stated that the equation

$\frac{L_n - L_1}{\log n}$ expresses the relation of the elongation produced by successive extensions to the same stress. In this equation,

L_n = Elongation at the end of the n th cycle

L_1 = Elongation at the end of the first cycle

$\log n$ = log of the number of cycles.

The same relation may be obtained by plotting these results on logarithmic cross section paper, the result being a straight line. The slope of this line is a measure of the cyclic fatigue.

Instruments for measuring the abrasion of rubber have not as yet proved very successful. The general method is based on the principle of subjecting a weighed sample of rubber to the wearing action of a rotating wheel, having an emery or carborundum surface, either for a certain length of time or for a certain number of revolutions. The sample is then reweighed and thus the weight of the rubber worn away is ascertained. For purposes of comparison it is generally reported in volume loss which is obtained by dividing the weight lost by the specific gravity of the stock. This test is of value with sole stocks as it gives a means of comparing different compounds for wearing purposes. One of the difficulties to be overcome in this test is the manner in which the pressure of the rubber against the surface of the wheel is to be controlled and maintained constant. At present it is attempted to regulate the pressure by means of a dead weight or a lever. Although neither one is entirely satisfactory, yet if either is watched closely the conditions can be kept the same and therefore the results are comparable.

A test for the purpose of learning something of the susceptibility of rubber to puncture is carried out on a machine for measuring the force necessary to puncture the stock.

The instrument is similar to the one used for testing the hardness with the exception that the plunger carries a sharper point than the one used for gauging the hardness. The force necessary to cause the point to penetrate the rubber is read directly from a dial graduated in arbitrary divisions.

No test with any degree of satisfaction has been devised for determining the liability of a rubber to tear.

Specific Gravity

Specific gravity or density, in our use here may be regarded as the weight in air of the sample divided by the weight of an equal volume of water at 4 deg. C., the maximum density of water.

Several general methods are in use for this purpose but we shall outline only four, namely, hydrostatic, floatation, pycnometer and Jolly Balance.

By the hydrostatic method a sample of any shape. is taken, having a weight of not less than five grams and its weight in air ascertained. It is then suspended by means of a fine wire or horse hair and then dipped into water. Air bubbles are removed from the surface of the rubber by going over it carefully with a camel's hair brush. This is necessary in all methods of determining density. A beaker of water is then placed on a support which straddles the pan of a balance. The piece of rubber is then suspended from the hook over the balance pan in such a manner that the rubber is immersed in the water when its exact weight is obtained. The weight of the horse hair immersed in the water must be obtained, then from the above procedure we have the weight of the rubber in air, plus the hair, minus the gross weight of the rubber and hair in water which will give the weight of the water displaced by the sample, or its volume. Since specific gravity equals weight divided by volume, we have the necessary data to obtain the density of the sample with reference to water at the temperature of the determination. If it is desired to make the temperature correction, all that is necessary is to multiply the specific gravity so found by the density of the water at the temperature of the experiment.

If it is desired to obtain the density of a sample lighter than water, it is necessary to use a sinker and its weight under water of course being known, the process is similar to the one given above. A piece of wire which is easily bent around the rubber serves this purpose very nicely.

The floatation method is good for control work in the hands of inexperienced workmen as it requires no weighings. It is based upon the principle that solids having the same density as liquids, when placed in them will neither rise nor sink and the density of the liquid is obtained by a hydrometer very easily. For samples with a gravity heavier than water, the density of the liquid is increased by the addition of solids which pass into

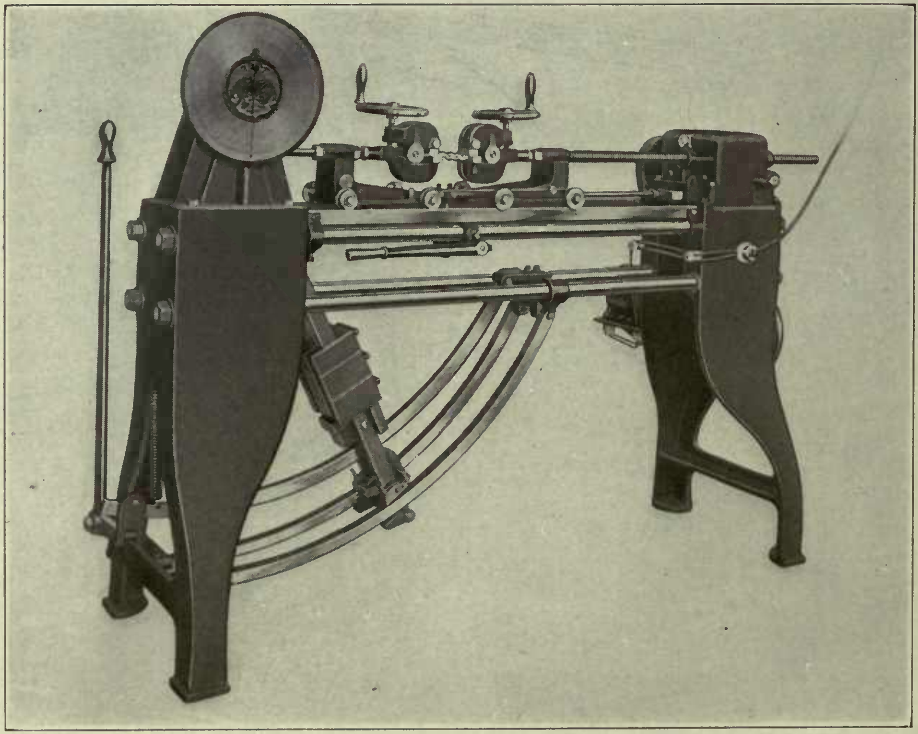


Fig. 55—Scott Model Q Horizontal Testing Machine

solution thus increasing the density. Zinc sulphate is used for such purposes. For instance, it is desired to produce a stock with a gravity of 1.42 and continue this for some time. A zinc sulphate solution may be made up to the density and kept indefinitely provided that from time to time it is tested and corrected, for its density will increase due to evaporation. All that is necessary, therefore, to check up the stock is to cut off a piece of the material, sink it into the solution and note whether it sinks or rises. This is a rapid control method only.

The pycnometer method is used largely for samples that exist as small pieces or powder, for they must be tested as powders. In some places the pycnometer is used altogether and the rubber to be tested is cut into narrow strips so that they will enter the bottle. This method is applicable to stocks either heavier or lighter than water.

A pycnometer bottle is carefully cleaned, filled with the liquid in which the density is to be determined, and whose density is known and represented by d. The filled pycnometer is then carefully weighed and this weight is represented by W. A certain amount of the sample is then weighed and is represented by W_1. This sample is then placed in the pycnometer and the bottle is carefully filled with the liquid and again weighed and the weight represented by W_3. We now have the data necessary for the calculation of the specific gravity of the sample.

d equals density of liquid used.

W_1 equals Wt. of sample in air.

W_2 equals Wt. of pycnometer and liquid.

W_3 equals Wt. of pycnometer plus liquid plus sample.

Therefore, the valume of water or liquid displaced is represented by W_1 plus W_2 minus W_3, and since Sp. gr. equals $\frac{\text{Wt.}}{\text{Vol.}}$, we have Sp. gr. equals $\frac{W_1}{W_1 \text{ plus } W_2 \text{ minus } W_3}$. Now if some liquid other than water were used or if we desire to make the temperature correction for water, then we must multiply the result so found by the density of the liquid at the temperature of the experiment, or it may be included in the above formula and it would stand thus: Sp. gr. equals $\frac{W_1 d}{W_1 \text{ plus } W_2 \text{ minus } W_3}$.

The Jolly Balance is a rapid method for the determination of the specific gravity and does not require the weighing of the sample on a delicate balance, thus making it possible for an inexperienced person to learn to carry on this test.

The zero point on the balance must first be determined, then any shape or size of rubber is taken and placed in the upper pan of the balance with the lower pan immersed in water. The beaker of water is then raised and lowered until the disc comes to equilibrium in front of the line through the mirror. The stage is fastened in this position and the reading made on the graduated scale. The sample is then removed from the upper pan and placed on the lower one, which allows of the weighing of it under water. The point of equilibrium is again determined and the reading is made. The zero point taken from the first reading represents its weight in air, W_1; the zero point taken from the second reading represents its weight in water, W_2; therefore, W_1 minus W_2 equals the water displaced and Sp. gr. equals $\frac{W_1}{W_1 \text{ minus } W_2}$.

This may also be corrected for temperature by multiplying the result thus obtained by the density of water at the temperature of the experiment.

Specific gravity has been and is of great value in determining the usefulness of a stock. Early in the industry it was considered that the higher the density of a compound, the less its merit, for pure rubber has a gravity less than one, therefore, as gravity increased rubber must have decreased. This is true within certain limits and today with the different practices of the compounder, more knowledge of a stock is necessary than simply its gravity.

Artificial Ageing Tests

The process of vulcanization increases the density of the stock and we, therefore, find that the specific gravity of cured rubber is always greater than that of the uncured dough.

These are the methods in commonest use in the laboratories today.

It is possible to learn a great deal from the results of ageing tests. As the term implies, the natural aging test requires a large amount of time before it is possible to obtain any results, therefore, artificial ageing tests have come into use. None of these artificial tests give all that is to be desired.

The one in largest use today consists of heat treatment. It is known that vulcanization takes place at all temperatures, and that its rapidity depends upon the accelerators used and also the compound to some extent. It follows then that if a sample is to be studied under certain conditions of elevated temperature the process of vulcanization is going to be continued. This will also vary with different stocks and thus comparative results from which to draw our conclusions are difficult to obtain. At least there is the possibility of being seriously misled.

Another point of difficulty arises from the fact that heat also tends to depolymerize the rubber. This is truer of some varieties than others; and is again a cause for a variance of results.

We know that cured stocks tend to oxidize. An increase of temperature always favors this process, and it has been estimated that an increase of 10 deg. C. will double the speed of the reaction, so it is perfectly clear that this influence must be taken into consideration. So we will mention two ageing tests that are studied under the influence of heat.

The first was proposed by Dr. Van Der Linde. He subjected the rubber to a temperature of 232 deg. F. for a period of two hours, thinking that in this time and at that temperature the ultimate cure would be reached. Then by studying the physical properties of the sample, such as its tendency to crack and its general appearance along with its tensile strength, set, and elongation as compared with a sample not subjected to the treatment, he was able to draw his conclusions. This has all of the objections mentioned above and then the cracking is only reliable in stocks that have a large amount of shoddy in them. The other heat treatment test was first used by Dr. Geer. He blew air through an oven held at a temperature of 160 deg. F. When this oven had become constant at working conditions, several samples of rubber 3/32 of an inch in thickness were placed in it. Three samples were removed every day for a period of two weeks. These samples were then allowed to stand for twenty-four hours until they had come to a state of equilibrium and were then tested for tensile strength and elongation. By this process the two sets of results were obtained and these were then plotted upon cross section paper. The curves thus obtained showed very clearly the time decay of the rubber. These were always compared against a standard stock which had been previously determined.

This test has the advantage over the other in that the temperature employed is much lower and thus the results of the criticisms mentioned above are reduced a great deal. Then, too, the possibility of interpreting the conclusion from a cure gives a better history of the stock.

The cures obtained by this method have been studied in comparison with the ones obtained from natural ageing tests with the same stock, and a close agreement is always found. Such a test has even been found to be of great value for a stock that is used in places where part of its service consists in simply being stored, such as fire hose.

Light Tests

Again, rubber articles have been studied under the influence of light. It has been pointed out that certain light rays injure rubber and should, therefore, be a means of testing rubber. No doubt the best test of this nature consists in subjecting the rubber to the direct action of the sun's rays. This enables one not only to study the effects upon the rubber but also to draw conclusions in regard to pigments used. This test consumes too much time to be of any great value and it must always be carried out in conjunction with a standard sample. To shorten the time for this test, high power artificial lights have been tried but have not proved satisfactory. It is a difficult thing to imitate the white light given off by the sun.

In carrying out the test the samples must not be displayed behind glass which will cut off some of the rays whose effects it is so desirous to obtain. As a result of this it is difficult to keep the temperature constant so that comparable results may be obtained at different seasons of the year. It is also known that drafts will influence the results. It will be seen that a great many difficulties lie in the way of this test.

Weather Exposure Tests

Subjecting samples of rubber to actual weather conditions is a very good test to establish one's opinion of a certain grade of stock. During the summer months especially, with frequent showers, and high temperature, a sample exposed to the weather undergoes about the severest test possible. Then it is possible to obtain comparable results, for two samples may be exposed side by side and one of them be a standard against which the other is to be judged. The presence of moisture in the air profoundly influences this test just as has been observed many times in the rusting of iron, which is a process of oxidation. A dry piece of iron rusts very slowly if at all, while a moist one changes rapidly. So it is with rubber compounds. It may be claimed that the test is too slow but during the summer in two months' time the results desired may be obtained. It is true that accidental compounds in the air may influence the results. For instance, if the samples are exposed to the weather in such a place that they come in contact with considerable sulphur dioxide, as it is thrown out of smokestacks, which, with the water in the air, forms sulphurous acid, thus in turn will oxidize to sulphuric acid and will produce its own effect upon the sample.

This is a test, however, which it is good to use.

To test rubber by artificial conditions we have in mind the carrying out of certain tests upon stocks, which, under the majority of circumstances, they will not encounter in their life history and yet to which they may be subjected at certain times.

For instance, it is well to see what effect certain road oils will have upon tread stocks as the tires may be used in a locality where the practice of oiling the roads is indulged in. Again, a machine standing in a garage may have its tires coming in contact with mineral oil and it is well to know what result such treatment will have upon the compound employed. In other words, it is a good practice to subject every stock, as far as practical, to artificial conditions, of a chemical nature approaching the actual conditions which the various articles will be subjected to in use. So the number of such tests is infinite and each workman should study his own problems and prepare and design his own tests.

Dielectric Tests

A knowledge of the dielectric power of a stock is of value for those working with stocks employed in insulating wires and in making gloves for men handling high tension wires. For this purpose it is only necessary to determine the voltage that will break through a stock of certain thickness and this is always stated in the specifications.

Viscosity Tests

Viscosity determinations have been tried as a means of determining the degree of vulcanization of stocks, but have never proved to be of much value. It is a test which may be used, however, to check up and keep cements uniform.

A very simple type of viscosimeter is obtained by taking a glass tube about one meter long with a diameter of ten centimeters. Place a cork in one end and then fill it with cement up to a certain mark. By means of a stop watch note how long it requires a shot to fall to the bottom. The time required compared with the time required for it to fall through a similar column of a standard cement gives the knowledge necessary to correct the one under consideration.

Friction Tests

In the making of pneumatic tires, the value of the finished product depends a great deal upon the friction employed. It is imperative, therefore, that some test be made to learn the relative value of different frictions.

The friction test is carried out on an ordinary tensile machine which is geared so that it is possible to run it at such a rate of speed that its jaws will separate two inches per minute. Then the machine must be equipped with jaws suitable to grip the friction test piece. If it is desired to test the friction in a tire, a cross section of it is made just one inch wide or close to that and then its width carefully gauged. The first ply of the friction is then separated a little distance and fastened in the jaws of the test machine. The pull necessary to separate the ply is then recorded on a chart and the pounds necessary to separate a strip one inch wide is calculated. A friction which requires twenty pounds pull to separate a ply one inch wide is regarded as satisfactory.

Each ply in the tire is tested out by this procedure.

When it comes, however, to testing the merits of one tire as compared with another, the most conclusive information is gained by putting them on a machine and running until one fails and then noting the mileage covered.

To get tests of value, they must be tried out in different parts of the country, thus obtaining different road conditions. Needless to say they should be used without chains. These actual service tests on what is known as test cars have been of great aid in perfecting the product of the tire industry of today.

Barbeque Test

When it comes to testing solid tires we have what is known as the Barbeque test. This test if properly conducted is of great service for it aims to give us knowledge at the point most critical in a solid tire, namely, the strength of the union between the hard rubber base and the tire itself. To carry out this test, the tire is secured in a vise, and, by means of a knife, an oblique cut is made through the tire down to the hard rubber base. By means of pulling and using the knife also, a separation of a few inches is effected so that it is possible to pull up the tire proper and tie a rope around it. This rope is then tied to a scale capable of recording the pounds pull and the pulling begun at a tangent to the point of separation. The number of pounds pull necessary to effect this separation of tire and base is carefully noted. The United States specifications require that for each inch of width at least 100 pounds of pull will be required to separate it.

This test has received severe criticism.

Solid tires are also studied under test cars and in working conditions. The rate of wear on solid tires is measured by taking the height of the tire from time to time and studying it with reference to mileage. This is best done by plotting the rate of wear against mileage.

It has not been our aim to even try to mention all the tests possible, but simply to give the reader an idea of how physical tests are studied and perhaps to suggest new lines of endeavor in this field.

APPENDIX

The Laboratories and Equipment of the Municipal University of Akron

Located in the center of the rubber manufacturing industry of the world, Buchtel College, now a part of the Municipal University of Akron, in the fall of 1908, installed among its courses the study of india-rubber and its use in industry. Dr. C. M. Knight, for thirty-eight years Professor of Chemistry in this institution, and to whom the present laboratory is dedicated, was the originator of the course. By virtue of his many years of teaching experience and his keen appreciation of the industrial demands of his city and country he had the wisdom to launch this work on a basis to insure success. He was of the firm belief that it was better to graduate a few men with a very high standard of ability than to turn out many with superficial knowledge.

In erecting a fine building the foundation must first be laid with care; so in securing an education that will permit of growth its foundation, too, must be deeply and carefully laid.

In the University of Akron course one full year is first given to the study of inorganic chemistry. The student thus becomes familiar with the great laws under which the science operates. The second year he studies qualitative analysis. Contrary to the requirements of a great many institutions, a full year of this work is required. A man has no license to be called a chemist until he is able to measure up as an analyst.

In the third year the student is mature enough, has technique enough, and is sufficiently grounded in principles to carry on quantitative analysis and begin organic chemistry. In this year he covers simply the paraffin series of hydrocarbons. At the completion of this, the foundation is laid for the study of rubber chemistry, for, in addition to having had chemistry, he has also had German and French, mathematics and physics, as well as courses in English and economics. The fourth year gives him the benzene series of hydrocarbons, rubber chemistry and advanced practical chemistry if he desires.

The Rubber Laboratory Equipment

The rubber laboratory is equipped to carry out all of the chemical experiments required in connection with the course. There is a rubber washer and mixing mill which is mounted on a large concrete base and driven by a motor. Another piece of apparatus is a steam generator with an automatic regulator. This furnishes the steam used in the press vulcanizer, and also the kettle vulcanizer.

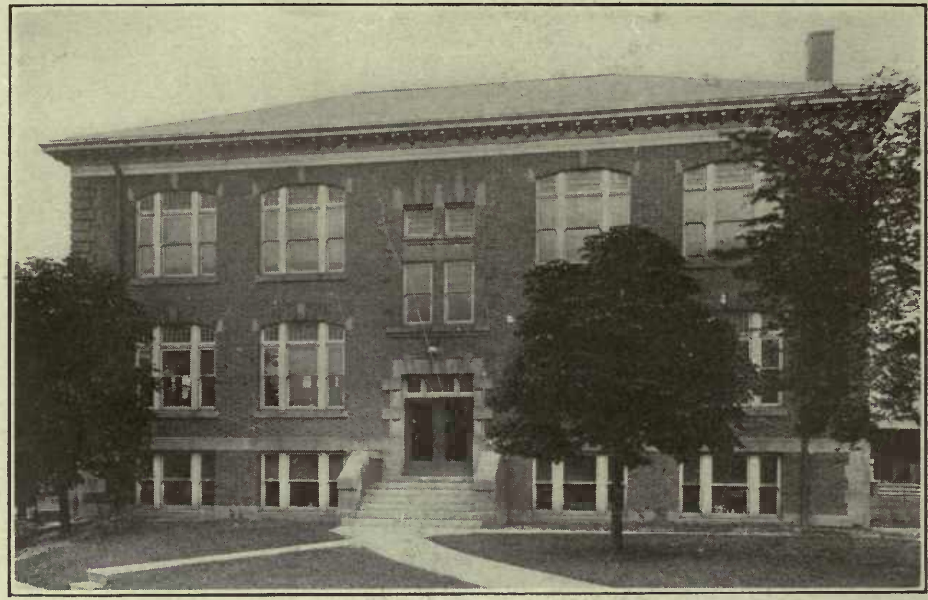
A Tinius Olsen testing machine forms part of the equipment.

With this outlay, it is possible to carry out actual work as the students will find it being done when they step into a factory laboratory.

Brief Description of the Course

Each subject naturally is composed of two parts: the lecture room work, consisting of lectures, quizzes, reports by students, etc., and the laboratory work.

In the lecture room, the history of the crude rubber is given and then its development is traced into a great industry. The different species are studied with reference to source, col-



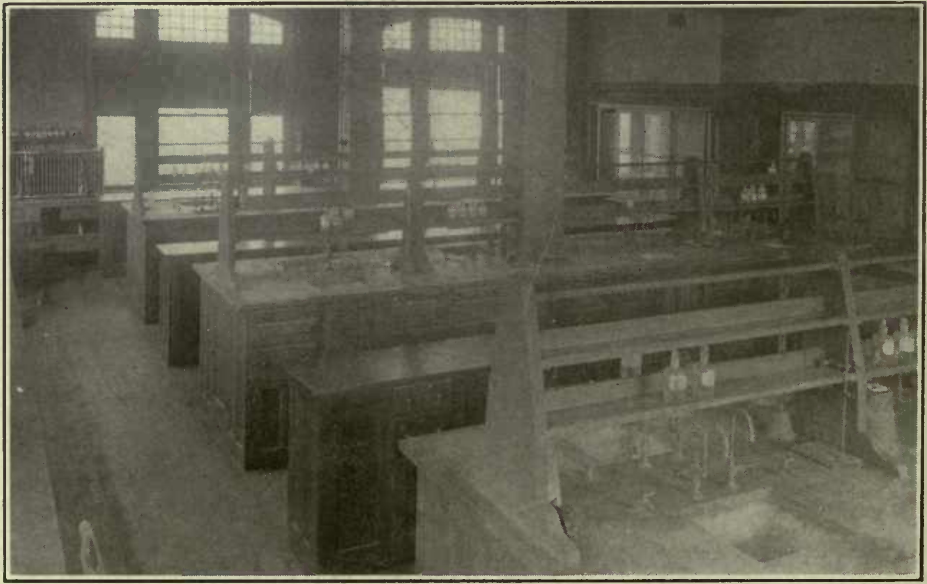
The Knight Chemical Laboratory

lection, coagulation, physical properties and use.

After some time is spent with the natural varieties, the plantation rubbers are studied. Here it becomes necessary to emphasize some of the principles of colloidal chemistry, by which many of the phenomena of rubber are explained.

After a discussion of the constitution of rubber, the different possible methods of procuring the synthetic product are presented. Methods of carrying out both the chemical and physical testing of the crude rubber are then given. This work completes the first half of our year's work.

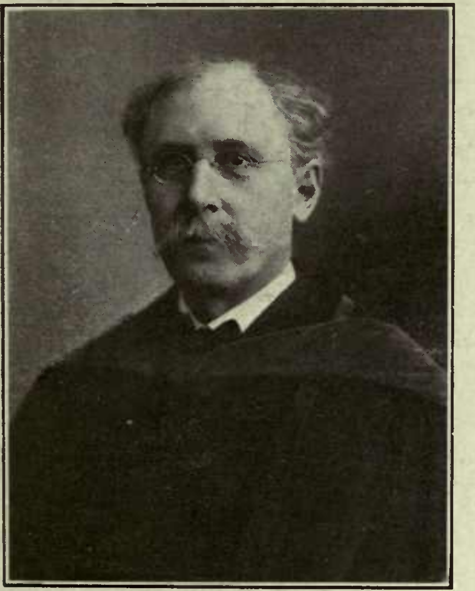
The second half is devoted to the adapting of this india-rubber to the various articles of manufacture. Here theory is presented with the practical side as well. In connection



One of the Laboratories

with this lecture room work, there is running the parallel laboratory work.

Beginning with the crude rubbers we study their peculiarities and their losses on being washed, likewise the action of different solvents on them. The fractional distillation of rubber is also interesting from a theoretical point of view at least.



Dr. C. M. Knight

Thorough analyses along all the different lines of work are carried out here. We are of the opinion that a chemist first of all must be an analyst and capable of doing consistent work along this line. This is accomplished in the first half year, leaving the second to study compounding and physical testing.

It should be stated here that great value to our men is obtained from frequent visits to the large factories here. After studying the washing of rubber, and carrying it out in the laboratory, it is very helpful to visit the wash rooms of two or more large concerns. This of course, applies to all divisions of the industry and, with the cooperation of the manufacturers of our city, we are able to study the various processes of manufacture in their factories.

Two Industrial Fellowships

Two industrial fellowships in the study of india-rubber have been established; one by the Firestone Tire and Rubber Co., and the other by the Goodyear Tire and Rubber Co. These fellowships are awarded to the graduates of first grade chemical courses anywhere. The Fellow receives three hundred dollars in money from the factory whose Fellowship he holds. At the end of a year he enters the employ of this company. The University gives him exemption from all fees but in return requires from him a maximum of twelve hours per week in way of laboratory supervision or correcting of note books or papers.