

THE UTILIZATION OF WASTE PRODUCTS

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A TREATISE ON THE RATIONAL UTILIZATION,
RECOVERY, AND TREATMENT OF WASTE
PRODUCTS OF ALL KINDS

BY
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TRANSLATED FROM THE SECOND REVISED GERMAN EDITION BY A
TECHNICAL CHEMIST

WITH TWENTY-TWO ILLUSTRATIONS

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PREFACE.

It is a matter of common knowledge that even to-day a large number of waste products are thrown on one side as useless, and either accumulate in large quantities if they are inorganic, or if organic they become exposed to the gradual decay which is inherent in them owing to their highly complex nature. Such substances treated in a rational manner would no doubt be capable of yielding a product, or in some cases a series of products, which would not only repay the cost of treatment but which might even equal or surpass the value of the primary manufactured article.

As an illustration of the truth of what has just been stated as well as the commercial or even national importance of the utilization of waste products, it is only necessary to point to the chemical industries in which the utilization of the various wastes is of the utmost value both from a sanitary and an economical point of view, and it is in these industries that we find the largest number of cases of the rational treatment of materials which at one time were regarded to be of no value. As a concrete example mention may be made of the rich treasures which have been derived from coal tar, not only the beautiful dyes which have helped to set the foundations of modern German chemical industries but also

the many synthetical drugs, essences, perfumes, and disinfecting products which are derived by various wonderful and ingenious processes from this very repulsive substance.

In these days it is more than ever necessary to give careful attention to what may at the present time appear to be valueless. Competition is so keen that even with the most economical—and therefore the most rational—labour it is difficult to make manufacturing operations profitable, and it is therefore only by utilizing to the full every product which is handled that prosperity for all may be assured.

In the revised edition of the present work the matter has been kept up to date; most new and approved methods of treating waste materials have been touched upon, but antiquated useless processes have not been included. It is hoped, therefore, that the work may continue to be a practical guide to those engaged in technical or industrial pursuits, who will perhaps find in its pages much that will be useful to them.

LONDON, *July*, 1918.

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THE UTILIZATION OF WASTE PRODUCTS.

INTRODUCTION.

THERE can be no doubt that a rational utilization of the waste matters which are produced so frequently and abundantly in the manufactures and industries is of more than ordinary importance.

Whilst we often find that some waste product is accumulating in such quantity as to injure and retard the continuous progress of a branch of industry, we also see, not rarely, that the rational treatment and utilization of such waste products either increases very considerably the general profits of an industry or even forms a separate and not inconsiderable source of gain.

The numerous communications, which have had as their subject the profitable utilization of waste matters, are usually only to be found scattered in the form of occasional communications through the vast bulk of technical literature, so that, under ordinary conditions, it would be impossible for most men engaged in technical pursuits to discover, from among the abundance of material, that which is especially interesting to them and which touches more particularly upon their avocations.

It is no easy matter to examine this abundant material, arrange it, excluding all that is doubtful and superfluous, and put the remainder in such a form that the practical man, engaged in a particular calling, may extract what is really useful.

Since the present work is the only one in the English language which for the first time treats fully of waste products in general and from a practical standpoint, omissions

may possibly occur; it is to be hoped, however, that any failings will be criticized in a friendly and well-meaning spirit. A smooth and well-trodden path may be traversed without danger even by an unsteady wanderer, but where the road must be first marked out and the rough path made smooth, progress is of necessity slow, and each step must be made sure before we extend to the next.

It is hoped that the present work on the Utilization of Waste Products will point out the way to those engaged in the various industries treated upon, and that it may act as a stimulant to still further advancements.

CHAPTER I.

THE WASTE OF TOWNS.

THE disposal of town refuse is one of the most important problems of present-day municipal engineering, to which a considerable amount of thought has been given, and which requires unremitting care and attention in order that the health of the community may be preserved.

Town refuse is of various kinds, most of it being included under the headings given in the tabular scheme below.¹

1. <i>Liquid refuse.</i>	2. <i>Municipal refuse.</i>	3. <i>Trades refuse.</i>
(a) Sewage proper.	(a) Vegetable offal or garbage from markets, shops and roads.	(a) Soil, rock, etc., from excavations.
(b) House slops.	(b) Ashpit refuse, including ashes, bottles and glass, old metals, old boots, wood, paper, etc.	(b) Old building materials.
(c) Road drainage.		(c) Manure from stables and roads.
		(d) Animal offal.
		(e) Dead animals.

Utilization of Town Refuse.—The chief exertions were first directed to extracting everything in any way useful from town refuse, and this was especially the case with regard to faecal matter which was and is even now in some places converted into manure; the rapid development of the large towns, however, compelled more attention to be paid to the quick removal of this material. Meanwhile the spread of hygienic knowledge and the experience gained during severe epidemics taught the municipal authorities that the health of the dwellers in large towns, especially in regard to the prevention of epidemic disease, depended largely on clean soil as opposed to a soil saturated with decayed and infectious material.

¹ H. De B. Parsons, "Journal of the Society of Chemical Industry," 1908, p. 376.

Thus the question of the utilization of town refuse became of secondary importance, the question of its disposal taking the premier place.

In some moderately-sized towns dry or earth closets are in use in which the faecal matter is mixed with waste shoddy or other material and after removal is allowed to dry spontaneously ; but so many difficulties were encountered in the manufacture of fertilizers from faecal matter, which, moreover, is subjected to so many precise and emphatic sanitary regulations, that, especially since it requires considerable capital, it has been superseded in large towns and cities by the water-closet system. This is in consonance with the ideas of the most prominent authorities on hygiene, who designate the latter method as the most suitable. The loss to agriculture of the manurial elements is more than counterbalanced by the efficiency of the method and the gain to the health of the community, while any doubts as to the advisability of the method may be met by proofs of the automatic purification of rivers.

In the majority of towns the sewage, house slops, and drainage water pass together into the sewers and are purified, either by settlement or by bacteria beds, the effluent being turned into the nearest stream or river, or, in the case of coastal towns, into the sea.

Attempts have been made in the past to utilize the useful constituents which it contains, but owing to the dilute state in which they exist this has not been attended with any success, therefore the object at the present time is to get rid of it as soon as possible after it has been sufficiently purified to do away with any risk of infection.

With regard to the solid matter the case is very different, the following methods of disposal having been tried :—

1. Tipping on land.—Where a sufficient area of waste land within easy access is available, most kinds of refuse can thus be got rid of, but with animal and vegetable offal this method is not suitable owing to the stench which arises. To obviate this difficulty trenches are dug in the soil and the refuse buried.

2. Tipping at sea.—This is only available at coast towns or those near to the mouths of large rivers, the material being taken out to sea in barges and there dumped.

3. Ploughing into the soil.—This is suitable for manure and garbage but not for the other materials. In some towns manure is collected from the roads and sold at a nominal figure.

4. Feeding to swine.—Applicable to garbage, but only locally.

5. Extraction of fat, etc.—Applicable to garbage and offal.

6. Destruction of organic matter by burning.—Applicable to practically all ordinary refuse.

In the United States of America and also to some extent in this country the garbage is treated for the extraction of fat either by the Arnold process, in which open steam is employed, or by the Merz and Simonin process, using a volatile solvent, usually coal-tar naphtha or petroleum benzine. The former method is the cheapest, though a lower yield of fat is the result. In either case the grease is dark coloured and of very low quality, its market value varying from 2-4½ cents per lb. The extraction of fat from garbage is by no means a remunerative operation, the only points in its favour being the saving of the fat from destruction and the keeping of a few "hands" in employment. According to Parsons, the following are the products obtained :—

Water and loss	85
Grease	3
Tankage	9
Tailings	3
	<hr/>
	100

In Brooklyn¹ the plant for treating garbage is of the Arnold-Egerton type and is situated at Barran Island in Jamaica Bay, to which the material is towed in barges and

¹Edward D. Very, "Journal of the Society of Chemical Industry," 1908, p. 378.

transferred by means of an elevator to the digestors. The digestors are large tanks holding approximately 8 tons each, closed with a cap which is bolted on during action. In these tanks the material is submitted to the action of open steam at a pressure of 80 lb. for a period which varies according to the nature of the product undergoing treatment. The vapour from the vats is condensed by a jet-condenser, the liquid thus formed being conveyed by a pipe to the sewers. After steaming, the pulpy mass is transferred to a tank which will hold the contents of four digestors, and from this it is delivered to frames covered with sacking in which it is submitted to hydraulic pressure, the water and oil passing through the sacking being conveyed by pipes into a settling tank below. In this the oil and water separate, the former being skimmed off and barrelled. The residue from the presses, or "tankage," is taken by a conveyer to the drying plant, and after drying it is passed through screens and then bagged. The value of this material is somewhat problematical; it is used as a "filler" for manures and contains small quantities of nitrogen, phosphoric acid, and potash, but burning would seem the proper end for it.

At this plant the garbage yields :—

Water	71
Rubbish	6
Tankage	20
Grease	3
									<hr/>
									100
									<hr/>

The removal and utilization of that waste of towns which may be described as household refuse, or "dust," is an important problem. In this case a process of complete and innocuous destruction is to be regarded as the ideal. From the politico-economical point of view, and for the sake of profit, it appears both desirable and justifiable to separate material of any value from the dust. The final solution of the problem will lie in the combination of the two endeavours: to extract from the dust what is still of value and convert it

into useful product, subsequently to destroy completely what is valueless.

In England and America household refuse is usually burned, the combustion taking place in special furnaces, called "destructors," according to the system of Freyer. Such furnaces burn all the refuse of a town, both dry and wet. It is said that, by means of the destructor, it is possible to burn dust to which a large quantity of inorganic, incombustible matter has been added. The furnace stands in a brick building and is fed from above. To the platform of the building leads a stage by which the dust-carts are brought up; they then deliver directly over the opening of the furnace. The dust gradually descends. It is in the first instance lighted by means of a small coal fire, and afterwards burns continuously. The material slowly falls farther and farther, finally reaching the part of the furnace at which the heat is most intense. The burnt residue passes through a grate into an ashpit, from which it can be easily removed. The installation consists of several furnaces in series in most towns six, but from eight to twelve are also found. From the hygienic point of view, it is important that the gases given off in the process of combustion should cause no nuisance to the neighbourhood. It has been found that the combustion is practically complete; however, in order to remove any unburnt gases which might be present, a smoke-consumer is attached to the destructor. The temperature in the hottest part of the furnace is very considerable; in the main flues it is about 300-400° C. An erection of this kind requires no great space.

In the immediate neighbourhood of London there are seven or eight destructors, some of which are within the boundaries and closely surrounded by houses. In Whitechapel, for example, the destructor is only 16 ft. removed from the wall of the nearest house, without injury to the inhabitants. Destructors are in operation in at least twenty-four English towns, and some have been in use for more than fifteen years. A furnace of this kind burns per week

(Sundays excepted) 24-35 tons—i.e. about 30,000 kilos. The cost of the process varies: in England it is estimated that it costs about one shilling to burn one ton of refuse, but in isolated cases the cost is reduced to about fivepence per ton. The products left after the combustion have many technical uses. Mortar and stone are made from them; at the same time the heat which is given out by the combustion of the dust is utilized, as, for instance, in driving compressed air installations, electric lighting, etc.

In this connexion it may be remarked that the household refuse of English towns is quite different in composition from that of continental towns, since in England coal is much more extensively used for heating private houses than in Germany.

Later, in 1894, further progress was made in the construction of destructors. The system is considered the best in which the destructor is composed of a group of furnaces in the form of cells, generally six in number, built of fire-brick, and covered by an arch which forms the top of the reverberatory furnace. The dust is emptied into an immense hopper at the top, from which it passes, after being rapidly dried, on to grates similar to those of boilers, in the lower part of the apparatus, where it is burnt. About every twenty minutes a fresh charge is let down and burnt. On the average, each cell of the destructor, in which the fire is never extinguished, burns from 30-35 tons of refuse per week. The ash and clinker from the furnaces are ground and mixed with one-third of their volume of hydraulic lime, thus forming a blackish cement, not of very agreeable appearance, but selling at eight shillings per ton, and used in buildings for staircases, and especially for drains. The specially valuable part of the process lies, however, in the utilization of the heat in the production of steam. With a good apparatus, each cell of the destructor gives ten horse-power, which is obtained from a boiler immediately attached to the destructor and heated by the hot gases. In twenty English towns the steam produced in this manner is used for disinfecting cloth-

ing and bedding. At Hastings the steam thus generated is utilized in pumping sea-water, which is used for flushing the public urinals and sewers, and for watering the streets. At Southampton the steam produced by the destructor compresses air, by which the sewage is raised and carried away; at the same time it generates energy for an electric lighting installation. In other places this power is used for driving chaff-cutters, for producing mortar and artificial manures, and for driving grinding and mixing machinery.

The table on next page by W. F. Goodrich¹ shows the working of destructors in various towns in Lancashire. The evaporative power of the refuse varies according to the nature of the material and the type of destructor used, ranging from $\frac{1}{8}$ to $\frac{1}{15}$ of that of coal. When the evaporative value is below $\frac{1}{10}$ that of coal the destructor cannot be regarded as a power producer.

The importance of the removal and utilization of dust at the present day, in view of the rapid growth of the great towns, is evident from the fact that in London, for example, not less than 1000 tons have to be removed daily. The experience of Hamburg is interesting; after the cholera epidemic an attempt was made to burn the refuse, and, following the example of London, a furnace for dust was erected. The experiment was favourable under the conditions then prevailing; the dust burnt alone, and only a small quantity of coal was required to start the combustion. Later, the dust could be burnt alone, but produced a rough and apparently valueless clinker. In Berlin a destructor was also erected, the experiences of London and Hamburg being utilized, and English workmen being engaged to build and work the furnace. Success in this case, however, was absolutely wanting, for there remained an incombustible residue amounting to 60 per cent. Thus, of 100 cwt. which were brought to, and had to pass through, the furnace, and which could only be kept burning by the addition of coal, 60 cwt. had again to be taken away. The municipal authorities

¹ "Cassier," 1901, 21, 99-122; also "Proc. Inst. Civil Eng.," 1902, 149 [3], 97-9.

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Town.	Evap. per lb. of Refuse.	Average Steam Pressure.	Temp. of Feed Water.	Consumption of Refuse per Cell in 24 hours.	I.H.P. per Ton on Basis of 20 lb. Steam Power per I.H.P.	Duration of Test.	No. of Cells or Grates in Use.	Rate of Consumption per sq. ft. of Grate per Hour.	Boilers in Use.
Oldham	0.880	lb. 128.0	F. 212°	1 cell = 7.96 tons	98.0	24 hr.	10 cells	lb. 25.0	2 Lanc.'s 30' x 8'
Ashton-under-Lyme	0.783	122.0	212°	" = 9.97 "	87.0	24 "	" "	31.0	2 Multitubular
Bury	0.532	122.0	53°	" = 9.0 "	59.554	4 "	6 "	33.6	3 "
Rochdale	1.78	114.0	212°	4 grates = 50 15 1 4	199.0	6½ "	4 grates	54.9	1 Lanc.'s 30' x 8'
Darwen	1.55	193.0	212°	" = 52 2 1 6	173.6	48 "	4 "	56.0	1 "
Nelson	1.516	118.0	212°	" = 61 0 0 0	169.792	9½ "	4 "	57.0	1 "
"	1.85	120.0	212°	" = 31 0 0 0	207.2	1 month	4 "	29.0	1 "
"	1.95	122.0	212°	" = 73 4 0 0	218.4	8 hr.	4 "	68.5	1 "
Blackburn	1.39	90.8	212°	" = 25 9 1 12	155.68	12 "	4 "	48.0	1 " 24' x 7'
Fleetwood	1.19	135.0	212°	" = 21 11 2 2	133.28	8 "	2 cells	80.5	1 Bab. & Wil. Tubular
St. Helens	1.54	127.0	212°	" = 27 12 0 8	172.48	7 hr. 20 m.	2 "	103.0	1 "
Warrington	1.14	68.0	104°	" = 23 0 0 0	127.0	24 hr.	2 "	88.48	1 "
Blackburn	1.297	122.3	212°	" = 11 3 0 12	145.264	7 hr. 40 m.	4 "	34.66	1 Heenan W.T.
Liverpool	1.173	122.3	212°	" = 16 10 0 0	131.376	24 hr.	8 "	62.16	4 "

were therefore compelled definitely to abandon the experiment.

In the next place, private industry stepped into the field. Several years ago a quite new method of disposal came into prominence, known as the "Budapest process". It requires large-scale arrangements for sorting the refuse, such as were installed at Budapest, combined with the burning of the combustible portions. The refuse is conveyed on an endless band, on either side of which children stand to sort the rubbish. One picks out green glass, another white glass, a third rags, a fourth bones, all of which are thrown into separate baskets behind the pickers. Then the contents of the particular baskets are collected, and everything still usable is disposed of.

In Berlin this method was rejected for sanitary reasons. Dr. Weil, an authority on sanitation, in a lecture to the Society for Public Health, stated that this so-called Budapest system, which was advanced in Berlin as quite novel, had already been forbidden in London by law in 1892. The advocate of the system could make no answer to Dr. Weil, whose statement still remains unrefuted, so that it may be accepted as correct.

The method employed for utilizing the household refuse of Munich at the large establishment at Puchheim, on the railway from Munich to Buchloe, is similar to the Budapest process. The author is obliged to the managers of this large establishment, now the third of the kind in Germany, for a complete insight into the method.

Every day two special trains, of thirty to forty waggons each, arrive in Puchheim from Munich. Each waggon contains four large trucks known as "harritsches". The refuse brought by these trains amounts to 450-500 tons daily, and is completely treated in ten working hours. The cost of railway carriage is about £18 per day, amounting to over £6000 per annum.

The "harritsches" are taken up by a lift from the waggons, they are emptied by the bottoms dropping outwards and are

then brought back. The contents of each truck are raked by a workman through a shoot, and then sieved. The fine sievings are used as manure, for which purpose there is a demand, since they contain no small amount of fertilizing matter. The price fixed by the management must be regarded as extremely low. The coarse residue then passes on to an endless band, from which, as in the Budapest process, it is sorted by women. The sorting yields a tolerable amount of usable material. There is, for instance, a considerable amount of glass, rags, bones, and paper, while even hare-skins are found in the season, and old shoes are also plentiful. About 500 or 600 bottles are collected every day. From the sorting band the residue passes into a sieving drum, which has meshes of various gauge. From the sieve the finer material, which is used as manure, is carried away by a screw conveyor.

The utilization of the refuse is here carried out in the most complete and rational fashion. Unbroken glass bottles are washed and cleaned by an iron bottle-washing machine, and are disposed of to the brewer, wine merchant, etc. Broken glass is also washed in an iron drum; it then goes to the glassworks. The countless rags are beaten in a special rag beater, by which they are opened out and freed from dust. They are then dried, disinfected, and sorted according to the nature of the fibre and the quality. The fine dust is mixed with phosphoric acid, saltpetre, and dried blood in a special mixer. The compound is then filled into sacks for use as a fertilizer. Old iron, which is also found in considerable quantity in dust, is converted into green vitriol. Old shoes are converted into ground leather, which is mixed with the fertilizer. Large quantities of tinsplate boxes can be treated in order to obtain the tin.

The works are plentifully supplied with steam-power, which is used for all the mechanical operations, and also for the electric lighting of all the rooms. There are about 3000 metres (nearly two miles) of railway track in the works.

The residue, which is absolutely unutilizable, is carried

away on rails in small trucks, three of which are drawn by an ox; hitherto it has been used for levelling the surrounding moor, but will shortly be destroyed by burning, the necessary furnaces being already erected.

From the sanitary point of view, the provision of lofty and airy working rooms, and several ventilating fans, has satisfied the demands of health.

The process of utilizing household refuse at Puchheim, which is allied to the Budapest method, is doubtless more rational, and may at the present time be described not only as the most important of the kind, but also as the best equipped and best managed.

The dust-melting process, based on the patent of Wegener, differs entirely from the above. In this process the refuse is fused at a temperature of about 2000° C. No sorting takes place, the dust, as it is removed from the houses, being emptied into the furnace, leaving it as a fluid glassy slag, which very quickly solidifies after it is run out.

This process certainly satisfies all the requirements of sanitation, but the question of cost remains to be solved. It has, however, been shown that the dust is fusible, leaving nothing but the above-mentioned slag. The cost ought not to be unsurmountable, since the householder has already to bear the expense of removing the dust and of its disposal. To reduce the cost as much as possible it is necessary to utilize the heat of the furnace gases, which reach the flue at 1250° C. Anyone acquainted with the subject knows that this heat can be utilized. It is only necessary to measure the temperature in order to be able to show how many horse-power per hour are available. According to measurements which have been made, the energy required in fusing the total refuse of Berlin would amount to 2800 horse-power per hour. There would be no appreciable difficulty in utilizing the waste heat; on the contrary, it is an important factor in calculating the cost of the process.

Various experiments have been made with a view to utilizing the slags, which constitute the residue in this pro-

cess of fusing dust. It appears to be best to temper the slag, which flows out, by gradual cooling, so that it is not excessively brittle. The slag has been powdered under stamps, and used as a substitute for emery. According to experiments its hardness is 9°, the same as that of flint. It is stated that this slag binds completely with cement, therefore, since the slag is quite fireproof, it may find employment in building operations, particularly for foundations. Taken on the whole, it is maintained that, according to previous experience, the fusion of dust would not cost more than the Berlin municipality now charge at their stations to the contractors for unloading—10 pfennigs per centner (about 1¼d. per cwt.). If the excess of heat were completely utilized, this cost should be considerably diminished. It should be observed that it is proposed to dispose of the residues or slag (which, as compared with the 60 per cent of Hamburg, only amount to 12 per cent) to glassworks, where they might be ground and mixed with the glass charge, but it is questionable if the glass makers could use it. It could at any rate be used as road metal.

In regard to the fuel, coal-dust firing is employed, as the intense heat can only be obtained in this way. A grate is consequently unnecessary, the coal dust being automatically projected from above by a special appliance. The dust at once takes fire at the high temperature and is converted into gases, the whole furnace being a mass of flame. No hearth is required, but only burning gases which fuse the dust. When this work is accomplished, they pass downwards to the flue, where the waste heat is utilized.

Above the furnace is a large opening for charging, provided with a double cover, which fits air-tight thus preventing loss of heat. For charging, the upper cover is taken off, the lower remaining closed; a box of dust is then emptied on the latter, almost filling the space between the two. The upper lid is closed, and the lower lid, the valves of which fall downwards, opened by means of a mechanism, so that the dust drops by its own weight into a pipe leading directly to the

furnace. In the furnace the combustion commences at a temperature of about 800° C., the dust being dried and all combustible constituents gasified, thus producing fuel for the fusion of the incombustible portion. From the furnace the unburnt dust, containing ash, crockery, iron, tinplate, etc., falls gradually on to a firebridge, where at a temperature of 1200-1400° C. some of the materials are softened and the others caused to sinter. Subsequently in the lower part of the furnace at a temperature of 2000° C. everything present in the dust fuses, and the liquid flows out continuously. The furnace is built of refractory bricks.

J. T. Fetherstone has given the composition of New York refuse as follows:—

Combustible.	Coal and Cinders.	Garbage.	Rubbish.
Carbon	55.77	43.10	42.39
Hydrogen	0.75	6.24	5.96
Nitrogen	0.64	3.70	3.41
Oxygen	2.37	27.74	33.52
Incombustible.			
Silica	30.01	7.56	6.49
Oxide of iron and alumina	8.98	0.41	2.03
Lime	1.21	4.26	2.26
Magnesia	trace	0.28	0.57
Phosphoric acid	nil	1.47	0.10
Carbonic acid	"	0.59	1.49
Lead	trace	0.20	0.52
Tin	trace sulphide	—	trace
Alkalies and undetermined	0.27	4.45	1.21
Calorific Value.			
Calculated	8382	7970	7250
Determined (average)	8510	8351	7251

The rubbish burns readily, developing considerable heat. A very high temperature in the furnace is required to destroy offensive matters, the temperature being at least 1500° F. The weight of the incombustible residue is about 33 per cent that of the original, but its volume is equal to 60 per cent. Artificial draught is required for the combustion.

The approximate calorific values of the refuse in B.T.U. per lb. is as follows:—

	Percentage Collected.	Calorific Value.	
		Material as Collected.	Dried Material.
Garbage	12.3	1800	8700
Ashes	63.7	1800	3000
Rubbish	6.3	6500	7500
Street sweepings	17.7	3600	7000

The mixed refuse has a calorific value of about 2913, being about $\frac{1}{4}$ that of coal. Trials were made in December, 1905, to estimate the amount of water evaporated by the burning of this refuse, at and from 212° F., 1.64 and 2.16 lb. of water being converted into steam by 1 lb. of the refuse. Subsequently trials by different observers showed evaporative powers of 2.28, 2.29, and 2.17 lb. of water per 1 lb. of refuse.

One or two examples of the working of ordinary destructors may not be out of place.

At Boun¹ a destructor of the type of A. Custodis and F. A. Herbertz was installed, the trials being very satisfactory. The installation includes seven destructor cells, the total capacity of which is 52,500 kilos of refuse per 24 hours. Special waggons are employed in collecting the refuse, these having loose doors in the bottom for discharging purposes. The refuse is taken on a transporter system to the storage bin, which has a capacity of 126 cub. m., and from which it is delivered to the cells by corresponding openings. The refuse is burnt on a grate with forced draught at an air pressure of 350 mm. water (= 14 in.). The rate of burning is equal to 313 kilos per sq. m. grate surface per hour. The hot gases from the cells pass into two large chambers lined with refractory bricks in which the fine dust carried off by the draught is consumed, and from thence pass to a water-tube boiler of the Babcock and Wilcox type provided with 108 tubes and having a heating surface of 220 sq. m. This boiler can also be independently heated by coal. The hot gases pass from the boiler to an economizer and thence to the chimney 40 m. in height.

The steam generated by the boiler is utilized for driving a turbine of 300 horse-power and a dynamo from which the

¹S. Bondot, "Elect. Rundt.," 1906, 23, pp. 331 *et seq.*

power is obtained for running the destructor plant. The two fans for producing the blast are driven by a 25 horse-power motor; these deliver 105 cub. m. and 130 cub. m. per minute respectively. The clinker from the cells is ground to a fine powder in a mill and sold.

A trial run with this plant in which 26,898 kilos of refuse were consumed at the rate of 2782 kilos per hour resulted in the production of 12,938 kilos of clinker and 3473 kilos of flue dust. The evaporative power was equal to 1.13 kilos of water per 1 kilo of refuse, the temperature of the flue gases 279° C., and the percentage of carbonic acid in the latter 8.8. On a three months' trial the evaporative power was found to be 1.05 kilos per 1 kilo of refuse.

At Burslem Electricity Works¹ a destructor of the "Heenan" type was installed. This has three cells which are charged from the front, their capacity being 33 tons of refuse per 24 hours. From the cells the products of combustion pass into a combustion chamber arranged at right angles to the cells, and from thence pass to a Babcock and Wilcox boiler, the capacity of which is 6000 lb. of water evaporated per hour at a pressure of 200 lb. per sq. in. The gases from the boiler are utilized for heating the air used in forced draught, the latter being produced by means of a fan driven by an electric motor. The official test carried out on 14 November, 1905, lasted 7½ hours, during which 26,572 lb. of refuse, mixed trade and domestic, were burned. The total grate area is 75 sq. ft., and the heating surface of the boiler 1966 sq. ft. The average quantity of refuse burnt was 48.8 lb. per sq. ft. of grate area per hour and the amount of water evaporated 49,990 lb. or 1.87 lb. per 1 lb. of refuse (actual) or 2.16 lb. from and at 212° F. The temperature of the feed water entering tank was 45° F. and the temperature of the combustion chamber 2032° F. The clinker amounted to 26.5 per cent on the refuse.

The Borough of Westmount, Canada, has a mixed refuse destructor plant, the results after eight months' working show-

¹ "Elect. Engin.," 1906, 38, pp. 294-6.

ing that 2000 lb. of refuse were equivalent to 283 lb. of coal in evaporative power. A trial in May, 1906, showed an evaporation of 1.36 lb. of water per 1 lb. of refuse, which compares with the average of eighteen European destructor plants reported by J. T. Fetherstone, the maximum being 2.66 lb., the minimum 0.88 lb., and the average 1.62 lb. water evaporated per 1 lb. of refuse.

NIGHT-SOIL AND SEWAGE MUD.

Utilization.—Although there are plenty of proposals for the rational utilization of excrement, yet hardly any process has succeeded in surviving. Thus Leube's process—the application of sulphuric acid—failed, and Petri's manufacture of fæcal stone could obtain no practical hold. The most rational method of treatment after the removal to a suitable locality, is to utilize it as manure. The preparation of an illuminating gas from excrement is described in the chapter on "Illuminating Gas from Waste".

In regard to other proposed methods, with the exception of the manurial, we give the opinion of Fischer.¹ "As a matter of fact, the application of human excrement as a fuel—Petri's fæcal stone—is the worst imaginable use to which it could be put since its most valuable constituents, nitrogen compounds, are lost. For large towns there is no other course than a well-arranged system of sewers and flushing."

Scott has patented the following process for treating sewage: The sewage, collected in a tank, is mixed with excess of caustic lime, the clear supernatant liquid being drawn off from the precipitate; in a second tank an iron or aluminium salt is added, which salt is converted into the hydrate by the lime present in the clarified water. The precipitate in the first tank, which contains the organic and inorganic matters suspended in the sewage, and to some extent also substances previously in solution, may be converted into cement or filter coke. The precipitate in the second tank, after calcination, gives metallic oxides which may be utilized. The water from

¹"Dingler's polyt. Journ.," 213, p. 269.

the second tank is sufficiently pure to be passed into a large stream, and, if it has previously been filtered through the coke obtained from the first tank, may even be run without danger into a small stream.

The sewage mud deposited by allowing sewage to settle in tanks is, whenever possible, pumped into vessels and sunk right out at sea. Trials have been made by the Royal Commissioners on Sewage for using this material as a dressing on land but without any useful results accruing. As a matter of fact, sewage mud is so finely divided that air can only with difficulty gain access, and on some soils, for instance clay or peaty soils, it would act as a poison. In Germany and to some extent in this country also the mud is treated with solvents for the extraction of the fat or grease which it contains, and quite a considerable quantity of such grease is thus obtained; though the latter is of very inferior quality it still has a distinct commercial value.

CHAPTER II.

BLOOD AND SLAUGHTER-HOUSE REFUSE.

Utilization of Blood.—W. L. Palmer employs blood to obtain a plastic material. It is passed through a fine sieve, dried, pulverized, then mixed with 20 per cent of bone meal and 10 per cent of size, placed in the required moulds and subjected to a high pressure at 120° C. This application of blood, and also earlier uses, in which blood and sawdust were used in preparing plastic masses, are now of no technical importance, since cellulose can at the present day be employed much more successfully in making artificial wooden ornaments.

Treatment of Blood.—The great obstacle to the use of blood in manufacturing processes is its tendency to decomposition, which rapidly occurs. This drawback may be obviated by carrying out all the operations as rapidly as possible. Heinson Huch of Brunswick has patented a simple process¹ for protecting blood from decomposition and drying it. According to this process the blood, in the vessel in which it is caught from the slaughtered beast, is stirred as it flows in with about 3 per cent of ground or finely powdered quicklime, i.e. about 450 gm. (one pound) for the blood from each bullock. After stirring for three to five minutes the mixture is allowed to stand. The lime rapidly settles to the bottom and the blood coagulates in a few minutes. It is then removed and placed in the sun in an airy position to dry, the drying being accelerated by stirring at intervals. In a short time the blood is dry; it remains free from smell and taste, and does not evolve ammonia. In the winter the drying must naturally be accomplished in a kiln, or a stove if the quantity

¹“Neueste Erfindungen und Erfahrungen,” 1877.

is small. The ground or powdered lime is brought into contact with all parts of the blood during stirring, unites with some of the water, and sinks to the bottom, leaving only traces in the blood, which becomes somewhat more alkaline and dries more readily, without clotting into masses, which occurs during ordinary evaporating. Since no smell at all is evolved, the blood retains the whole of its nitrogen, which is of considerable importance in considering its value as a fertilizer.

G. Thenius has also described the practical treatment of blood.¹ Bullocks' blood is that which is obtained in the largest quantity in slaughter-houses. In order to obtain it in a readily fluid condition, it is stirred with a stick for some time until the fibrin has separated in long threads, when the stirred blood is brought on to a fine hair-sieve and washed with water. The washed fibrin is placed on dry cloths, so that it may rapidly be freed from water, as otherwise it quickly decomposes. After this operation with dry cloths has been frequently repeated, the fibrin is placed on a hair-sieve and dried at 120° C. in an air-bath. It is to be observed that this fibrin still encloses some globulin, and cannot therefore be regarded as pure. The globulin and also hæmoglobin, the colouring matter of blood, are always enclosed by the fibrin; they may be removed by long-continued washing in order to obtain pure fibrin.

The blood freed from fibrin does not decompose so rapidly and may in cold weather be kept for several days. The author treats the fluid blood mainly by two methods:—

1. By drying upon flat zinc sheets (previously oiled), the edges of which are turned up to prevent the fluid from running off, this being done in drying-stoves, provided with shelves, in which the temperature is maintained at 30-35° C. The dried blood, which is now in the form of thin, transparent sheets, is used in sugarworks, under the name of blood albumin, for clarifying the juice. From 100 parts of the fluid blood about 21-22 parts of the dry substance are

¹ "Neueste Erfindungen und Erfahrungen," 1878.

obtained; thus 78-79 per cent of water has to be evaporated. The author has constructed a special furnace for the drying-stove, the arrangement of the flues in which has been found to be very effective; a regular heat being maintained, with economy in the expenditure of fuel (Fig. 1).

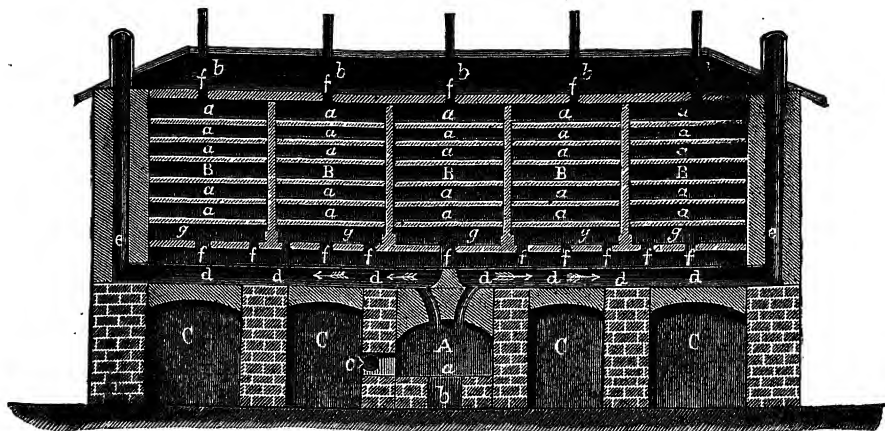


FIG. 1.—Vertical section of the furnace, with drying-stoves for heated air. *A*, Furnace; *a*, hearth; *b*, ashpit; *c*, door; *d*, flues; *e*, chimney; *f*, air passages; *g*, covering plates. *B*, Drying-stoves; *a*, shelves; *b*, pipes for the moist air. *C*, Workrooms.

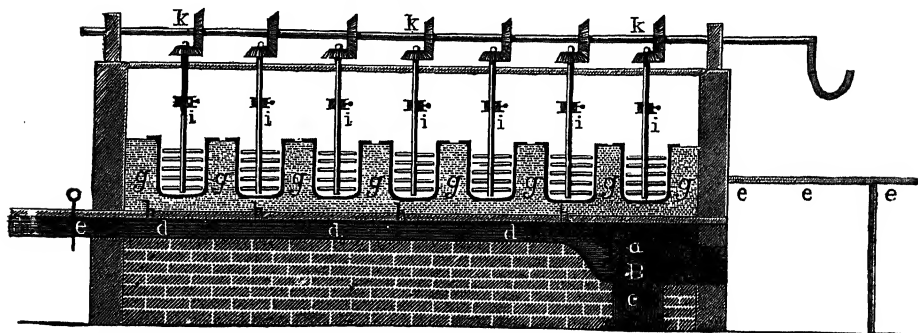


FIG. 2.—Longitudinal section of the furnace used in making dry blood meal.

2. By thickening the fluid blood in pots with continuous stirring, in order to obtain blood meal. The author has constructed for this purpose a special furnace (Fig. 2), which has

proved very satisfactory. In the figure, *a* is the fireplace, *B* the grate, *c* the ashpit, *d* the flue; the chimney, *f*, which receives the flue, is regulated by the damper, *e*. The flues are roofed with cast-iron plates, *h*, upon which is a sand-bath, *g*, containing the iron vessels in which the stirrers, *i*, can be kept in motion by the shaft, *k*. Round the furnace is a platform shown at *e*, to facilitate the removal of the pots and the actuation of the stirrers by a labourer.

The fluid blood is brought into the pots, which should only be half filled; they are then placed in the sand-bath and the stirrer *k*, *i*, put in position. The furnace is heated and the stirrers set in motion, in order that the blood, which soon coagulates, may not adhere to the walls of the pots and char. With continuous stirring, the mass, which was at first pasty, gradually assumes a pulverulent condition; it acquires thereby a dirty brown colour, which turns to reddish brown as the drying proceeds. The vapours evolved during this period have a peculiar odour and oxidize metals, such as copper, very rapidly. The workman in charge of this operation is considerably affected if he should breathe these vapours, especially when fresh blood is being treated. As soon as the pulverulent blood has become quite dry and no more vapours are evolved, the stirrers and pots are removed from the sand-bath, the pots emptied into sheet-iron vessels which can be securely closed, and the contents allowed to cool. When quite cold the blood is perfectly dry and can be readily ground. The average yield is 20·5-21·2 parts from 100 parts of fluid blood, so that it may be assumed that at least 78·8 per cent of water and volatile matter are lost during evaporation. When the blood, whilst still somewhat moist and powdery, is filled into strong linen bags and subjected to a considerable pressure in a press, there is obtained a watery and fatty liquid, the fat of which solidifies at low temperatures and can be separated from the water. The quantitative yield of this liquid is 2·7-3 per cent. The aqueous solution contains the salts. The solid compressed residue is more adapted for storage than the blood meal, since it does

not absorb moisture. The dry blood may either be used for producing prussiate of potash, or for obtaining a very good charcoal containing nitrogen, but more particularly for enriching artificial manures.

The apparatus shown below (Fig. 3) is used in making blood charcoal. The dried and powdered blood should not more than half fill the cylinder, since the mass swells on heating, and the stirrer, *B*, must always be kept in motion. The cylinder (Fig. 4) is made of cast iron or thick sheet iron and is constructed so as to be capable of removal from the furnace

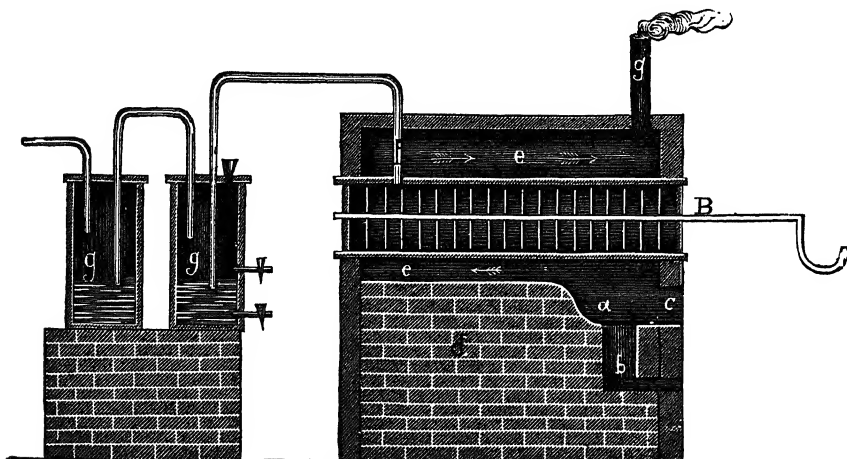


FIG. 3.—Longitudinal section of a blood charcoal furnace. *a*, hearth; *b*, ashpit; *c*, door; *e*, flue; *f*, exit-pipe; *g*, chimney.

d. The stirrer, *B*, can also be removed together with the lid from the apparatus, in order to facilitate cleaning.

The vapours evolved, consisting chiefly of ammonia and empyreumatic oils, pass away by the pipe, *f*, to the receiver, *g*, which contains a leaden vessel, in which is placed dilute sulphuric acid. The ammonia combines with the acid to form ammonium sulphate, whilst the oily substances float on the surface and can be utilized as Dippel's oil. Fresh dilute sulphuric acid must frequently be supplied to the receiver, *g*, after drawing off the saturated ammonium sulphate solution.

As soon as vapours cease to be evolved from the apparatus, the cylinder is removed from the furnace, allowed to cool for several hours with frequent stirring, then opened, and the fine blood charcoal brought into a vessel which can be tightly closed. This charcoal absorbs gases with such extraordinary rapidity that it may spontaneously heat up and become red hot. In medicine this preparation is known under the name of *carbo animalis*; it is used principally for dusting malignant wounds, which give off much bad gas and smell. When freshly burnt, it could be used for the disinfection of hospitals and similar buildings and is a valuable decolorizing agent.

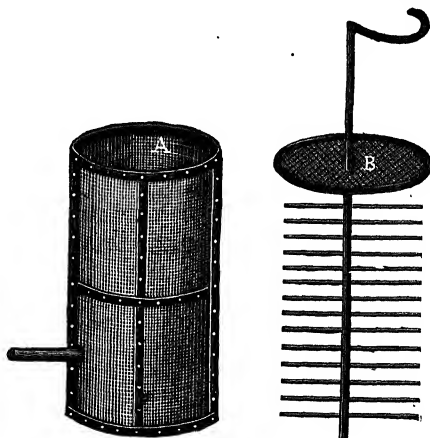


FIG. 4.—A, Cylinder for blood charcoal.
B, Lid, together with stirrer.

If blood charcoal be ignited with potash it acquires much greater decolorizing power; for this purpose the charcoal is preferred in a granular form, in which state it is much more porous.

The most important technical use of dried blood is in the manufacture of potassium cyanide.

If dried pulverized blood or blood meal is allowed to lie exposed to the air, it rapidly attracts moisture from the atmosphere and gives off ammonia. This formation of ammonia takes place more rapidly if the blood meal is mixed with finely powdered aluminium silicates—as, for example, brick

dust—and at the same time freshly burnt wood charcoal in powder is added. The mixture soon becomes warm, the heat increasing with the thickness of the layer. The addition of wood charcoal prevents the loss of ammonia by condensing the gas in its pores. On this account the addition of charcoal to artificial manures which contain blood meal is much to be recommended, since then no loss of nitrogen occurs. If blood meal be mixed with dry earth, an increase in temperature and evolution of ammonia can be distinctly observed. If moist earth be used, the blood meal is quickly decomposed, an action which may be still more accelerated by adding alkaline substances, such as wood ashes. Accordingly it is advisable, before using dried blood as a fertilizer, to mix it with wood ashes and powdered charcoal, and to apply it to the ground in wet weather. The decomposition and action of the fertilizer then take place very rapidly. Blood manures are hence very valuable in agriculture, especially since the food they contain can be very quickly conveyed to the plant in soluble form. The author has made experiments on vines and kitchen vegetables, in which very good results have been obtained. For one vine 140 grms. (about 5 oz.) of dry blood meal, mixed with double the weight of wood ashes and charcoal, are sufficient. This mixture is mixed to some extent with the soil of the vineyard, and is also placed in the pit, where otherwise stable manure would be used. A great advantage of this system of manuring lies in the saving of labour, since one man can readily manure in a day several hundred vines.

The following is an analysis of dried blood:—¹

Water	10.56
Nitrogenous Organic Matter	86.92
Saline Matter	2.52
	<hr/>
	100.00
	<hr/>
Nitrogen = Ammonia	17.24

It should be remarked that the fertilizer, mixed with an equal weight of sieved wood ashes, may be kept or packed in

¹ Stevenson Macadam, "Journ. Soc. Chem. Indt.," 1888, p. 95.

well-closed vessels, e.g. in casks lined with tinfoil, but better still in empty petroleum or oil barrels. It should be well pressed down, so that there are no interstices; the atmospheric air then cannot act on the blood meal. The mixture must also be kept dry, in order that there may be no loss of ammonia.

Preparation of Albumin from Ox Blood.—The blood caught from the slaughtered animals is allowed to coagulate in dishes, when the albuminous liquid rises to the surface and can be poured off. During this process the dishes are kept in a cool place, where the separation more readily occurs. The so-called "blood-cakes," which separate, are transferred to a linen filter and gently squeezed, in order to obtain the remaining albumin which they contain. The residual fibrin is then cut into lumps and dried in drying-chambers on zinc plates. The blood-albumin is now treated according to the method described for drying the fluid blood, by bringing it in very thin layers upon zinc plates with turned-up edges, and freeing it from water in a drying-chamber at a temperature which does not exceed 30-35° C. The zinc sheets are previously greased with a little olive oil, in order that the dry albumin may be more easily removed. To free the dried albumin as far as possible from other matters which adhere to it, distilled water is poured over it. After some time this is drawn off; it contains the readily soluble phosphates and other impurities. The residue is now mixed with warm distilled water and frequently stirred, when the blood-albumin dissolves. The solution is filtered through flannel, which retains the impurities and the colouring matter of the blood, the filtered concentrated solution being again brought on to the zinc sheets and dried in the drying-stove at 30-35° C. The principal applications of blood-albumin is in calico-printing, for the fixation of the colours and also for leather dressing.

Edmund Campe, of Brünn, has related certain very noteworthy experiences in the practical manufacture of blood-albumin.¹ In order to obtain a very pale blood-albumin, it is necessary to use the greatest care in catching the blood from

¹ Wittstein's "Vierteljahrschr. f. prakt. Pharm.," 1872.

the slaughtered cattle and sheep, the vessels for clearing the serum and the sieves being placed as near to the slaughter-house as possible. When possible, the serum should be drawn off in the slaughter-house itself, or the immediate neighbourhood, and the blood should be brought on to the sieve not longer than 30 to 60 minutes after it is caught. The freshly-curdled blood is cut into cubes of about 1 in. square, brought upon the sieve, and allowed to drain for 40 to 48 hours. After the lapse of this time, the clear serum is drawn from the clearing vessels, with the precaution that none of the red colouring matter deposited at the bottom is removed with it. In order to avoid this, Campe employs clearing vessels with somewhat concave bottoms, and has the orifice of the exit pipe about $\frac{1}{8}$ in. above the bottom.

After all the clearing vessels are emptied, the whole of the serum is placed in a tub of soft wood, about 3 to 4 cwt. in capacity. The tub, which is wider at the top than the bottom, has a wooden tap about 2 to 3 in. from the bottom. The further treatment of the serum varies, according as "natural" albumin, i.e. without shine, or "patent" albumin—which shines—is to be made.

In order to obtain natural albumin, it is only necessary to add $\frac{1}{4}$ lb. of (spirits of) turpentine to each cwt. of serum, and stir well for an hour. For this purpose Campe uses a circular board, about 1 ft. in diameter, perforated with holes, and fastened to a stick. After stirring, the serum is covered and left 24 to 36 hours at rest. The turpentine rises to the surface, together with a greasy, greenish white fat. The clarified serum is now drawn off through the wooden tap near the bottom. The first runnings, which are always somewhat turbid, are rejected, the remainder of the serum being taken to the drying-stove for evaporation. Campe evaporates in iron trays, 12 in. long, 6 in. wide, and $\frac{3}{4}$ in. deep, which are painted with enamel, varnished, and stoved. The temperature of the drying-stove, when the serum is poured into the trays, is about 50° C.; when the trays are

full, the temperature may rise rapidly to 52 to 55° C., which is maintained for two hours, without opening a ventilator. After this time all the ventilators are opened, and the temperature allowed to sink to 50° C., at which it is maintained until the end, the ventilators being opened, in order to ensure the replacement of the moist air. In order to promote a rapid renewal of air, Campe employs air-holes in the masonry at the bottom. The exits are naturally at the top, and open above the roof.

In order to produce from the serum the so-called "patent" albumin with a handsome glitter, Campe takes for each cwt. of serum $6\frac{2}{3}$ drm. of oil of vitriol and $6\frac{1}{4}$ oz. of strong acetic acid (sp. gr. 1.04), mixes the two, and, after standing for one hour, dilutes with about 6 lb. of water, and then pours in a very thin stream into the serum, whilst constantly stirring. Next $\frac{1}{4}$ lb. of turpentine is added per cwt. of serum, and the mixture well stirred for 60 to 90 minutes. After the serum has stood 24 to 36 hours at rest, the clear portion is drawn off as before, and ammonia added to weak alkaline reaction before placing in the drying-room, in order to neutralize every trace of free acid. The plates are rubbed with warm tallow, so that the finished albumin may easily be removed from them.

By this treatment only a portion of the albumin is extracted from the blood for the preparation of the so-called primary albumin. Now comes the manufacture of secondary and tertiary albumin. The second variety is more an accidental manufacture, for which only the serum of those vessels can be used which for any reason has acquired a reddish colour. Campe also took for it the last pale red liquids obtained in drawing off the serum for primary albumin. The treatment for secondary albumin is the same as that given for primary. Tertiary albumin is the last product; it is used in sugar refineries in considerable quantity. The cubes of blood which remain upon the sieves are brought into a vessel with a false bottom about 8 to 12 in. up and bored with $\frac{1}{2}$ in. holes; water is poured on in sufficient quantity;

also all the residues from the primary albumin are added—i.e. the red deposit which formed in the settling vessels, the whole being well worked up with the hands. The liquid which collects below the perforated bottom is made slightly alkaline with a little ammonia, and brought into the drying-stove. This product also glistens, and is the so-called tertiary albumin.

The blood, which remains behind in the double-bottomed vessel, is then passed (according to Campe) between two toothed rollers, working together, so that a uniform paste is obtained, which is dried at 60-75° C. in a stove built with shelves. The sheet-iron drying-trays used in the stove are 2 ft. long, 1 ft. wide, and about 1½ in. deep. The use of this product is somewhat extensive. In order to improve it as a fertilizer, Campe mixes it with solid human excrement and ground oak galls and moulds it into bricks, which are dried in the air, and finally ground in the manure mill. The product is known as blood-manure: it contains about 6 per cent of nitrogen, and is particularly efficient for grasses and leguminous plants.

Preparation of Fibrin and Butyric Acid.—The fibrin obtained in the form of threads by whipping ox blood is washed with distilled water until it appears quite white, and the blood corpuscles have been removed. It is then rapidly freed from water on linen cloths, as before described, and dried on hair-sieves at 120-150° C.

If the moist fibrin be treated with pyrolusite and sulphuric acid, butyric acid is formed, which may be used in the *manufacture of butyric esters*.

Butyric acid is also prepared as follows: 80 grms. of moist fibrin, 320 grms. of starch, 20 grms. of tartaric acid, and 5 kilos of hot water are mixed together; then 1.5 kilo of sour milk is stirred in, and the mixture left for forty-eight hours in a warm place at 32-36° C. until fermentation commences. When the fermentation has become active, 520-550 grms. of finely powdered chalk are added and the whole frequently stirred. At first calcium lactate is formed and the

mass solidifies, but after a time it liquefies, and in about fourteen days the formation of calcium butyrate is practically complete. The process is finished when bubbles of gas cease to be evolved. The liquid is then filtered through cloth, and sufficient sodium carbonate added to convert the calcium butyrate into sodium butyrate and calcium carbonate. The latter is filtered off and the liquid evaporated. To the residue sulphuric acid is added, equivalent in quantity to the sodium carbonate; the butyric acid separates while sodium sulphate remains in solution. The butyric acid is again neutralized with soda, and the butyrate decomposed by sulphuric acid in a glass retort and applied, when colourless butyric acid distils over.

In order to obtain butyric ester from the butyric acid, two parts of alcohol are mixed with two parts of butyric acid, and one part of strong sulphuric acid added. An oily layer separates upon the liquid; it is washed with water, shaken for some time with magnesia, filtered, and dehydrated by means of calcium chloride. It is finally distilled from a glass retort, when a water-white, very mobile liquid is obtained, of a penetrating odour similar to that of pine-apples. The specific gravity of the ester is 0.913; it boils at 113° C.

Butyric ester is principally used in making imitation rum. It is mixed with the proper quantity of rectified spirit, acetic ester, vanilla essence, and water—in the last of which sugar-candy and caramel are dissolved, in order to give the rum the necessary colour. A very good formula is—for 50 litres of rum—500 grms. of finest rum essence, 100 grms. of butyric ester, 100 grms. of acetic ester, 50 grms. of essence of vanilla, 150 grms. of essence of raisins, 30 litres of high strength spirit, and 30 litres of water. In the water dissolve 1 kilo of sugar-candy and 250 grms. of caramel; mix the whole well, and allow to settle for several weeks.

Butyric ester is also much used in compounding fruit essences, e.g. of raisins, apricots, strawberries, etc., which are again mixed with spirit and other ethers in various proportions.

Utilization of Animal Offal.—Animal offal is sometimes dried and sold as a manure. The following is the composition of a sample of this material:—¹

Moisture	6.48
* Nitrogenous organic matter	26.77
Alkaline salts	3.42
Phosphates	45.68
Carbonate of lime	12.61
Silica	5.04
	100.00
* Nitrogen equal to ammonia	4.41

Fat from Animal Offal.—The oldest method of obtaining fat from animal offal consists in heating the material in a boiler over an open fire. With this method, in order to avoid disagreeable odours a simple expedient may be adopted, according to Terne.² When pans heated directly by fire are employed, they must be covered by a sheet-iron lid in such a manner that it does not interfere with the workman stirring and skimming off fat, and, on the other hand, the pan must be tightly closed during the intervals. When a pipe through the lid is brought into communication with the ashpit of the boiler-fire in a proper manner, the disagreeable vapours in passing through the fire will be partially decomposed, and partially diluted with the fire gases, so that they reach the atmosphere through the chimney unperceived. If the offal is boiled, as is almost universally the case, by steam in wooden vessels, the objectional odours may be removed in a simple manner as shown in the annexed sketch (Fig. 5) which is self-explanatory.

The conditions are different when flesh is boiled by means of high-pressure steam. According to Terne, the simplest and best method for removing the objectionable gases and vapours is the following: The mixture of gases from the closed boiling kettle is first subjected to the full heat of the boiler fire in a superheater, built of fireproof materials, placed in the boiler flue. From this superheater Terne takes the

¹ Macadam, "Journ. Soc. Chem. Indt.," 1888, p. 84.

² "Chemiker-Zeitung," 1879, No. 11.

gases, when possible, along both sides of the boiler fire in a hollow space built of fireproof materials, one side of which forms a wall of the fireplace, the other side being in communication with the atmosphere through short pipes. The superheated gases enter this retort-like space, mix with the atmospheric air, and then the mixture enters the firebox of the boiler. The gases being in a highly heated condition and well mixed with the oxygen of the air, on meeting the fire are burnt with absolute certainty. It is to be remarked that the best apparatus may work without effect if the gases from the kettle are blown off suddenly under great pressure and with the cock full open. In boiling a kettle, the exit

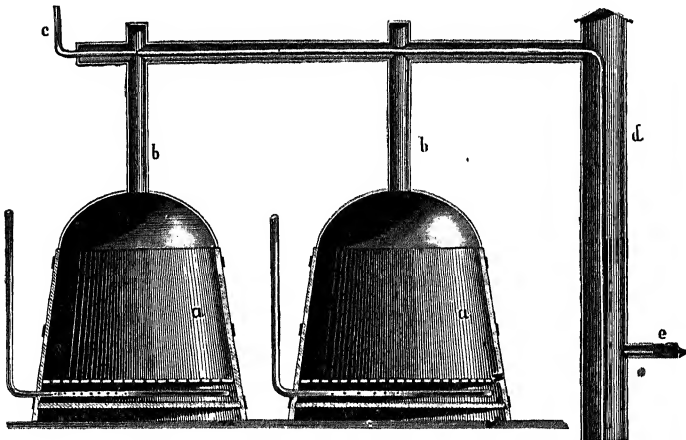


FIG. 5.—*aa*, pans with perforated false bottoms and perforated pipes for direct steam; *bb*, pipes connecting with a large pipe; *c*, condensing pipe carrying a current of water; *d*, condensing tower with water-pipe; *e*, steam injector to create the draught.

pipe must be left open until the boiling point is reached. When boiling actually begins, the cock is closed and the kettle raised to the pressure at which it is intended to work. The kettle should be allowed to stand at this pressure for about an hour; then, whilst still admitting steam, the blow-off cock is cautiously and partially opened. With careful management it is possible to keep very near the original pressure. If the gases are removed slowly at regular intervals

they may be destroyed without fail; but if with the cock full open they are allowed to rush suddenly, at the full pressure of 2-3 atmospheres, into the combustion chamber, a considerable proportion will naturally escape unburnt into the air.

Extraction of Glue from Animal Waste.—According to Terne's communication on the manufacture of glue,¹ slaughter-house material may be arranged, according to the proportion of glue it contains, as follows—(1) ox feet, (2) pigs' feet, (3) calves' and sheep's feet, (4) raw bones, (5) ox and pigs' heads.

The material is freed as far as possible from blood, this being easier the smaller the state of division. For this reason the larger works have machinery for tearing up the fleshy portions and breaking up the bones. The best bone-breaker, according to Terne, is that of Baugh & Son, of Philadelphia.² When the material has passed through the breaking machine, it is most advisable to free it from blood and dirt in a suitable washer. After removing the blood, Terne treats the material in suitable wooden vessels, which must be well covered, with a saturated solution of sulphurous acid. The duration of the action varies according to the nature of the material; experience alone is the only guide by which it is possible to determine the amount of action proportional to each kind of material and the season of the year. This results in a considerable improvement in the colour. The material, after steaming, produces a clear, almost colourless liquid, which, upon evaporation in vacuum pans, gives a glue in no way inferior, either in colour or lustre, to the best hide glue. The fat of yellowish bones is at the same time perceptibly bleached, besides which the unpleasant smell usually accompanying bone fat is entirely removed.

For the production of sulphurous acid, Terne has devised a simple apparatus, which has been found practically successful (see Fig. 6). The coke towers are erected in such a position that the outer wall is warmed by the heat of the boiler-house, and thus the whole is protected from the frost.

¹ "Dingler's Journ.," 1876, p. 253.

² *Ibid.*, 1869, p. 186.

In consequence of the treatment with sulphurous acid, portions of hide, as well as the sinews, swell, the latter acquiring a silky lustre and becoming transparent like gelatine. The tissues which yield the glue are not only bleached, but also become much less compact. In consequence of this treatment it is possible both to shorten the time of the boiling, and also to work at a diminished pressure.

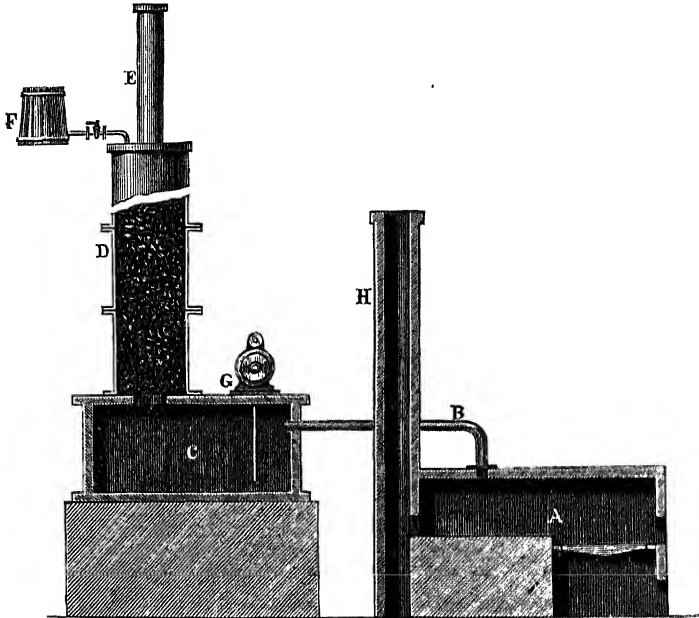


FIG. 6.—A, Sulphur burner; B, stove exit pipe; C, collecting tank; D, coke tower, consisting of twelve earthenware pipes, each 760 mm. (30 in.) long; E, draught regulator; F, water tank; G, steam pump for acid; H, chimney to sulphur burner.

The washed and bleached raw material, after treatment with the sulphurous acid, is ready for boiling. The chief conditions for the production of good strong liquors are low pressure and the shortest possible duration of boiling. The boiler erected as shown in Fig. 7 satisfies all the conditions required for regular, gentle boiling, and affords a certainty of obtaining a product almost free from fat. The pipe *F*,

for direct steam, is only employed for bringing the water rapidly to the boiling point; the closed coil *B* is sufficient to keep it boiling. After boiling and settling, the fat is run off through the pipes *K*₁-*K*₅.

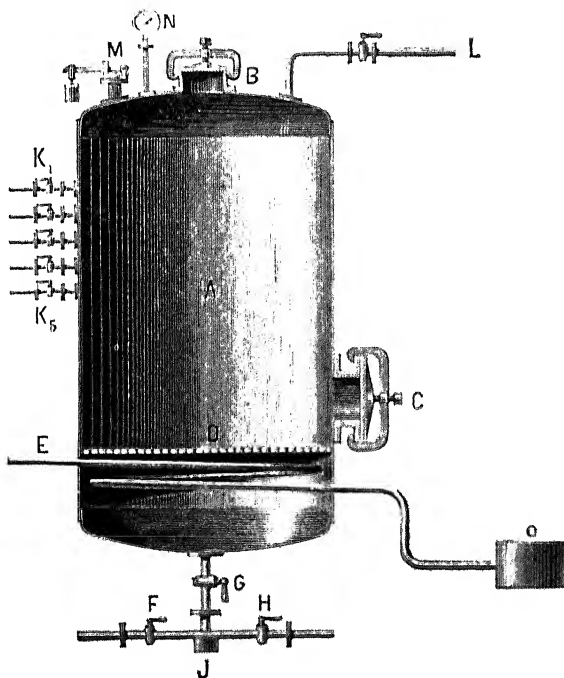


FIG. 7.—*A*, iron pan, lined with lead in order that the bleaching process may be conducted in it; *B*, feed opening; *C*, outlet; *D*, perforated bottom; *E*, steam coil connected with the steam trap *c*; *F*, steam pipe; *G*, drain cock, shut during boiling; *H*, cock on drain pipe; *J*, water outlet; *K*₁-*K*₅, run-off cocks for fat and oil; *L*, pipe conveying the noxious gases to the boiler fire; *M*, safety valve; *N*, pressure gauge.

The liquor, completely free from fat, is now filtered, for which purpose Terne employs a bone-black filter filled to a height of about 1.22 metre (4 ft.). The bone-black is covered with coarse sacking, and the whole filter is surrounded by a steam jacket. Probably a filter press would be more suitable. From the filter the liquid is taken to the vacuum pans. The

consistency of the size obtained in the vacuum pans varies considerably according to the purpose for which it is intended and the temperature of the air; it is impossible to lay down general rules. However, the size is boiled down to such a consistency that as soon as it sets on cooling it is capable of being cut, or the glue, cast into plates, is readily and quickly removable from the moulds. Strong tinned sheet-iron plates are the most suitable for the moulds, but they have the disadvantage of readily warping. In order to avoid this, glass tables made for the purpose are employed; they impart to the glue a very fine lustre, but the fragility of the glass plates is a decided drawback.

Every manufacturer has to give the greatest attention to the cooling of the glue; whenever possible it is cooled to a temperature of 0-5° C. In order to accomplish this, all the large works in America are provided with refrigerators and cooled working-rooms. For glue which is to be cut, Terne has found moulds of strong galvanized iron about 3 mm. thick ($\frac{1}{8}$ in.) the most suitable. The moulds are about 254 mm. (10 in.) high, the upper opening is 305 × 356 mm. (12 × 14 in.), and the bottom 290 × 330 mm. (11.5 × 13 in.). When a refrigerator is not employed, the glue in the moulds may, with great advantage, be cooled by placing in a tank of running water. Moulds constructed of bad conductors of heat are absolutely to be rejected, since they retard the setting and render the glue liable to decomposition.

The plates of glue, cast or cut out of the moulds, are dried on wire netting. For the sake of economy in netting, Terne hangs the plates, after they have attained a certain firmness, vertically from thick iron wires.

The bones, hoofs, horns, hides, and hair of animals are also utilized, as will be described in subsequent chapters. There has also arisen, especially in America, quite a number of subsidiary industries to the slaughtering of animals, or what is known as the packing-house trade, in which a number of therapeutical preparations are manufactured. These include pepsin, pancreatin, trypsin, bone marrow,

rennet, hæmoglobin, oxgall, etc., besides the cleaning and picking of entrails to be used as sausage skins, etc., nothing being wasted. The residues from all these operations go to the manure house to be converted into fertilizers.

Handling Bones for Glue Stock.—According to the “National Provisioner” bones are first heated with steam under pressure which dissolves out all the fat and glue, the former being separated by skimming after standing. The bones are then ground for use as a fertilizer. When the bones are to be used for manufacture into knife handles, buttons, etc., they are cooked with water in open vats at a temperature of about 200° F., whereby the fat is melted out but little of the glue is removed. Horn piths are washed and dried and then cooked for glue, which is much esteemed for size purposes.

The feet of oxen, after removal of the hoofs, are cooked in water. In their fresh state they form an excellent food known in some places as cow heel. The liquid from this operation is allowed to stand when an oil rises to the surface. This is skimmed off into cans, allowed to stand, then carefully decanted from the water and flocculent material which has settled out. It forms an excellent oil for lubricating and other purposes, being known by the name of neat’s-foot oil.

Waste hide pieces are also treated for the preparation of glue. If they are of fine quality and quite fresh the product obtained from them is gelatine.

Fat and glue can also be obtained from the liquid in which hams have been boiled. Where this is not possible, however, the liquid should not be thrown away, as when mixed with solid food it forms an excellent food for pigs.

Utilizing the Offal of Animals.—Very little offal from animals is now wasted. The blood is collected and treated in various ways. Usually it is dried and added to manures, but some of it is treated for the manufacture of blood albumen, the fibrin being removed and the liquid portion evaporated. Blood is also converted into sausages.

The entrails of animals are converted into sausage skins,

for which purpose they are thoroughly cleaned, scraped, and preserved in salt brine. The entrails of sheep and goats are converted into strings for musical instruments.

From the stomachs of oxen is obtained pepsin, from the pylorus is produced pancreatin. Enzymes are also obtained from the liver, kidneys, spleen, etc., while the gall (oxgall) is used by designers for removing the greasy feel of oiled cloth.

CHAPTER III.

FAT FROM WASTE.

Recovery of Neat's-foot Oil.—The fresh feet of oxen, calves, and pigs are boiled in a pan with water; the boiling is continued for fifteen minutes, after which the heating is moderated, so that the liquid is no longer in ebullition. The fat, which collects as an oily layer on the surface of the hot water, is continually removed by means of a shallow spoon, and collected in a tall, narrow vessel. The residue in the boiling vessel—the feet freed from fat—is disposed of to glue manufacturers. On long standing, the neat's-foot oil separates on the surface of the water in this vessel as a clear oily layer, which is poured off from the water, and brought into small bottles of white glass, which are exposed to direct sunlight in order to bleach the fat. According to R. Brunner,¹ the bleaching is more rapid if a sheet of violet glass be placed in front of the bottle, for violet light has the most powerful action. The finest product is that which has been separated by freezing. The neat's-foot oil is, with this object, exposed to the intense cold of winter, and the residual liquid portion separated in the cold from the solid portion by pressing through fine linen cloth. In France, sheep's feet are first immersed in water heated to 75-80° C. for about twenty minutes, when wool and hoofs may easily be removed by hand; the feet are then boiled with steam. Four hundred sheep's feet give 1-2 litres of fat (0.22-0.44 gal.) of 0.915 specific gravity.

Recovery of Bone Fat.—Bones are not rendered unsuitable for the purposes of glue or bone-black making by the

¹ "Die Fabrikation der Schmiermittel," A. Hartleben, 1897.

removal of the fat. For this purpose the fresh bones are brought into a pan and covered with water, which is very slowly heated to boiling. The boiling is continued for several hours, and the mixture then left at rest. After five to six hours the crude fat has collected on the surface; it is removed, whilst still fluid, into a wooden tank lined with sheet-lead.

The best refining agent for this fat appears to be the so-called *aqua regia*, which is obtained by making a mixture in a glass vessel of one volume of white nitric acid and four volumes of strong hydrochloric acid, and allowing it to stand until it has acquired a reddish yellow colour and evolves a penetrating smell of chlorine. Not more *aqua regia* should be made than can be used within a few days, since it soon loses its activity. To 100 parts of fat contained in the above wooden vessel is added 1-1.5 part of *aqua regia*, which is mixed with the fat by prolonged stirring, and remains in contact with it for some hours. When the bleaching is finished, warm water is added, and the acid then run off carefully through a plug-hole at the bottom of the tank. The fat is again mixed with warm water, well stirred, and the water drawn off. This washing with warm water is repeated until the last trace of acid is removed, i.e. until the water does not act on blue litmus paper. It should also be mentioned that the lead sheets, with which the vessel is lined, are at first strongly attacked. The white coating produced on the lead—lead chloride—is not removed, since it protects the lead beneath from the further action of the acid in the same manner as a varnish.

When older bones are used, the above method for obtaining the fat is somewhat altered. The bones are boiled with water, as above described, a brown fat of unpleasant odour being obtained, which is drawn off into wooden vats and allowed to stand for several days. During the slow cooling, a granular greyish-white mass separates, upon which floats a brownish yellow oil. The solid portion may be used in the manufacture of ordinary soap, the liquid in the preparation

of lubricants. The fluid portion of the bone fat is bleached with *aqua regia*, as above described. The older the bones, the larger is the quantity of *aqua regia* required. The addition of any larger quantity than that mentioned above is, however, not desirable; after 1 per cent has been added, each fresh addition should not be more than 0.25 per cent. Finally, in order to free the bone fat from any oleic acid which may have been formed, it is treated with about 10 per cent of its weight of caustic lime, which is slaked with water immediately before use, and the resulting milk of lime stirred with the fat and then allowed to settle. The oleic acid is thereby completely removed by the lime. Pearlash may be used for the same purpose. According to Brunner's experiments, the oleic acid may also be removed by an addition of litharge (lead oxide), especially if the fat be warmed before the introduction of the litharge. The lead oleate, which is produced, remains mixed with the fat, and converts it into a mass of the consistency of hard salve, which may be employed as a very useful lubricant for waggon axles.

A considerable amount of bone fat is also extracted by solvents in a similar manner to that described below.

Recovery of Oil from the Cleaning Waste of Machinery.—

The most suitable method for the recovery of the oil is founded on the fact that all the substances used as lubricants are soluble in petroleum ether and benzene. The lubricant is dissolved in one of these solvents, and obtained by evaporation of the latter. The solvent is also regained, and may again be used for cleaning a fresh quantity of cloths.

The used waste is squeezed fairly tight into a sheet-iron cylinder, provided with a tap at the bottom, and with an air-tight lid. Before the lid is put on, so much petroleum ether or benzene is poured over the cloths that, after they are saturated, the solvent quite covers them. The lid is then put in place, and the vessel left at rest for 12 hours.

The solution of the lubricant is then brought into a distilling apparatus, the still of which is heated by an open or closed steam coil. Since both the solvents mentioned have

a boiling point below that of water, they distil completely, and can be regained by cooling the vapours. The lubricant, which was dissolved from the cloths, remains in the still in a fluid condition and is run off from a tap at the bottom.

The waste is also heated in a still to recover the last portions of the solvent, and the waste is then sent out for use again. There are firms who will quote prices for waste to be returned to them in its dirty state after use for the recovery of the oil.

In order to renovate cleaning cloths saturated with fatty lubricants, the method of saponification may be employed. The cloths are brought into a pan, weak caustic soda solution poured over and heated to boiling. From time to time a few cloths are taken out of the liquid to see whether all the fat is yet saponified. When this is the case, the cloths are removed from the liquid, and boiling continued, when an ordinary soap is obtained. Cloths saturated with mineral oils or paraffin cannot be cleaned in this manner, but must be treated with the above-mentioned solvents.

Utilization of the Fat obtained in Glue-Making to obtain a Solid Lubricant.—The raw material from which glue is made is generally waste matter, such as the waste of slaughter-houses and tanneries, bones, rabbit and hare skins from which the hatmakers have stripped the fur, also cat and dog skins, ox feet, calves' and sheep's feet, sinews and entrails. These substances receive a preliminary treatment with lime, in order to remove particles of blood and flesh, which would hasten decomposition and give the glue a dark colour, and also in order to saponify the fat. For this purpose the substances are treated in large pits or tanks with thin milk of lime for 15-30 days, during which time the lime is often renewed. When this has been done, the adherent lime is removed from the animal substances, which are worked up for glue.

The residue, which, in addition to lime, contains the fatty matter of the substances treated, saponified by lime, is known as "glue fat". The cheap lime soaps, which can be bought

under this name, may with advantage be used in preparing machinery greases. The process of preparing such greases is as follows : The lime soaps are placed in a pan, which they half fill, and then heated over a gentle fire until they melt. The fire is then gradually increased and the boiling continued until the mass has been so far boiled down that a sample, brought on to a sheet of glass, can be drawn out into long threads on touching with the finger. In order to determine the right point, tests are frequently taken during the boiling, since, if the mass thickens too far, it cannot be used, and will be wasted. Thick mineral oil is now added gradually in small portions, and with continual stirring, until the desired consistency, which is tested by taking out portions on to a glass plate, is reached. The mass is then run into a tub and stirred until nearly cold.

Since glue fat contains so many impurities—dirt, hairs, etc.—it must previously be cleaned, which is best combined with the melting process—the dirt swimming on the top being skimmed off and the deposit which collects at the bottom removed.

Utilization of Cotton Seed.—At one time cotton seed was a waste product and was either dug into the ground or burnt and the ashes treated likewise, but now cotton seed is a valuable product worth about £8 10s. per ton decorticated or £5 undecorticated (pre-war prices), owing principally to the oil it contains, which even when crude has a market value of about £30 per ton at the present time. The oil is extracted by hydraulic pressure from the crushed seed after steaming, the yield being about 15 per cent. The residual cake is still valuable for cattle feeding, yielding £4 10s. to £5 per ton (pre-war prices). It contains about 5-10 per cent of oil and 20-40 per cent of albuminoids. The ground seeds and other oil seeds are, however, sometimes extracted with solvents, as for instance carbon tetrachloride, for the removal of the whole of the oil, when the residual meal is of no value for cattle feeding and can only be used for manure.

The cotton seed now produced in the United States is valued at 50 million dollars per annum.

Oil from Maize Germs.—In the manufacture of starch from maize or Indian corn there is an accumulation of a large quantity of the seed germs which are removed by the sieves after crushing the seed; these contain about 25 per cent of oil and were at first wasted; they are now, however, pressed for the recovery of oil, which appears in the market as maize oil and is a valuable product, while the residue goes into cattle cakes.

The residues from most oil seeds are similarly converted into cakes either alone or mixed with other ingredients (compound cakes), only those containing poisonous or disagreeable ingredients being unfit for this purpose. This has created an enormous trade, and is one of the best examples of the utilization of waste products.

Oil from Wine Residues.—After expressing the juice from the grapes the residue consisting of skins and seeds is turned out of the presses and usually dug into the ground or burnt. The seeds can easily be removed from the skins by washing through sieves, and as they contain oil this is worth extraction. According to F. Rabak in a United States Bulletin there are 90,000-120,000 gals. of this oil annually available, and trials of it have shown that it is a good drying oil which may be used in place of linseed oil.

The recovery of oil from the waste waters of wool washing works is described on p. 121, and of oil from tanneries on p. 50.

Reclaiming Motor Grease for Fuel.—The grease removed in the daily cleaning of the wheels, axles, and other parts of motor-omnibuses and the paraffin which was used for cleaning them are utilized by the London General Omnibus Co. in a manner described in the "Commercial Motor". In cleaning with paraffin, both paraffin and grease were wasted. The omnibus parts to be cleaned are now placed in a cradle in a hot solution of caustic soda and boiled. This removes the whole of the grease, which rises to the top and is collected with a wooden rake. The cradle with the parts is then put into a second tank of boiling water, which finishes the clean-

ing. The grease is treated at a central depôt, and provides sufficient fuel to drive two 80 h.p. Diesel engines and leave some over for sale. Oil rags, instead of being thrown away, are now put into a centrifugal steam-heated chest. This process extracts all the grease and oil, which runs off into barrels. The rags are then washed and used again.

CHAPTER IV.

TANNERY WASTE.

Utilization of the Waste as a Fertilizer.—Opinions have been expressed against the use of spent tan bark as a fertilizer on account of the tannin it contains, which might injuriously affect cultivated plants. Still it may be remembered that all barks used for tanning purposes are completely extracted. In an article in the "Mark Lane Express" the above opinion was pertinently refuted. The tanning process, it is there said, gives rise to a quantity of waste and residues, which may very well have unrestrained use in agriculture—in fact, to a much greater extent than was formerly supposed possible. These residues are divided naturally into animal and non-animal. Agriculture can with advantage employ only those residues which are not capable of being utilized in any other way, since one could not pay the same price for fertilizers as for a material out of which something useful could be directly produced. The animal waste of tanneries is much richer in manurial substances than the non-animal. In tanneries the fresh raw hides are first subjected to the prolonged action of milk of lime; they then undergo two operations, which determine the value of the tannery waste. In the first place, the hair is removed from the outside of the hide, and then remains for a long time in contact with lime. The second manipulation consists in removing the adherent flesh from the inner side of the hide, and also the thin cuticle. These waste matters are mixed together, and lie in heaps. They contain on an average about 75·5 per cent of water and 24·5 per cent of dry matter; the latter is composed of 84·5 per cent of organic constituents and 15·5 per cent of mineral substances.

In 100 parts of the mineral matter are contained 3.25 parts of silicates, 17.5 parts of calcium phosphate, 69 parts of calcium carbonate, and about 10 parts of other salts. The mean proportion of nitrogen is about 7 per cent. Generally these heaps are from two to three months in collecting, during which time they lose about one-fifth of their volume of water and three-tenths of their nitrogen. This loss is due to the rapid decomposition of the animal matter by bacterial action assisted by the lime. This fertilizer has then, according to present prices of its proximate constituents, a value of 24-40 pfennigs. In strawberry plantations the soil is covered by a layer of tan bark about 2 inches deep. The fruit has then a clean bed, and the snails, the chief enemies of the strawberry, are kept off.

The vegetable portion of this tannery waste is a result of the tanning, which is only obtained after the hides have undergone their first treatment. This process is accomplished by using the bark of oaks or other trees rich in tannin, which is finely ground or powdered, and then put in alternate layers with the hides in the tan-pits, water being then run in to dissolve the tannic acid.

The loose and fibrous nature of spent tan bark leads to the experiment of using it in place of *straw for litter*. When so used, it absorbs double its weight of liquid; it is advisable for this purpose to use it together with straw. It is not heavy, and may therefore readily be carried about. Tan bark, however, always still contains a certain percentage of tannin, and it is recommended to use it in combination with lime, phosphates or ashes, materials which at the same time hasten its decay. In combination with animal excrement, tan bark accordingly forms a valuable fertilizer. In gardens it retards in the most marked manner the evaporation and drying of the soil.

Finally, there is known the utilization of bark to form *bark cakes*, which are made in a press and used as fuel. Tan bark is also used, on account of its elasticity, for covering the floors of gymnasia, etc.

✓ *The Waste Waters of Tanneries in their Application as Valuable Fertilizers* is advanced by J. S. Schultz in his "Leather Manufacture". We follow here the views laid down by Schultz, as communicated to the "Gerberzeitung" by F. Kathreiner, of Munich.

The water used in softening, as also from the lime-pits and tan-pits, which have become useless, and the wash waters from the scouring and cleansing operations, are all collected in a large tank placed below the level of the tannery, so that all these valuable liquid fertilizers may be collected without pumping. This reservoir may be at some distance from the position where the washing and scraping operations are performed; in fact, it is an advantage if it be several hundred feet away rather than near at hand. It should be of sufficient size to contain, not only the waste waters, but also the solid matters which come from the sweepings and cuttings on the floors of the washing and drying places. These waste waters are so valuable that the author can see how a small tanner could fertilize 100 acres with the waste of a tannery treating 5000 hides. Exhausted bark, fine cuttings and scrapings, and even earth, may be brought into this reservoir, in order to take up the ammonia, and then be added to the soil with great profit.

✓ *Waste, consisting of Pieces of Untanned Hide, and of "tawed" leather,* may be used in the preparation of the finer kinds of glue. On account of the differences in the material the waste from untanned hides and from leather is collected in separate vessels. The waste of "tawed" leather, if it has been sufficiently dried by exposure in thin layers, may be stored, without further treatment, in any vessel until a sufficient quantity has been collected. The waste from untanned hides may be treated in the same manner, but it is not dried, since the skins, being saturated with water, are precisely in the condition which allows of their easily being converted into glue. The glue maker would have to soften the dried waste, and labour would be thus lost. The hide waste is therefore left in the swollen state, care being taken that it

does not decompose. This is done by keeping it in a tub under clear lime water, sufficient to cover the cuttings and also containing sufficient lime. Fresh lime water is therefore added from time to time. When the tub containing the cuttings is placed in a cool room, they may be kept for four to six weeks without decomposition; if they are then to be worked up for glue, the lime water is run off and the hide washed several times with pure water.

It is still more convenient to keep the hide cuttings in a weak solution of carbolic acid—1 in 1000. When they are to be used, they are taken out of this solution, allowed to drain, and washed with water. The carbolic acid solution may be used to preserve fresh quantities of hide.

Hide clippings may be converted into glue without further treatment. The clippings of "tawed" leather are best treated repeatedly with cold water, and then with hot water, in order to "untan" them and, as far as possible, to obtain the original hide. Clippings of chamois leather can only with far more difficulty be converted into glue, since in them the tanning substance is far more firmly combined than in "tawed" leather. It is best to boil these clippings with weak caustic liquors, by which they are at least partially untanned.

In order to convert into glue the clippings of leather tanned with alumina soaps, they must first be boiled in a liquid containing an acid, such as sulphuric, in order to decompose the insoluble soaps. The clippings are then squeezed and boiled with a weak caustic lye, in order to convert into the soluble condition the free fatty acids thus liberated.)

Recovery of Oil from Chamois Leather Manufacture.—The fatty ("stuffed") waste of the tanner and currier is utilized, according to J. Bergmann,¹ by the following process: One end of an ordinary barrel, best of hardwood, is removed, the barrel placed with the open end upwards, and a perforated false bottom is inserted at a height of 15 cm. (6 in.) above the

¹"Neueste Erfindungen und Erfahrungen," 1894.

bottom. A steam-pipe of 13-20 mm. bore (0.5-0.8 in.), according to the size of the barrel, passes down in the barrel to below the perforated bottom; a valve for regulating the supply of steam is placed above the barrel. The waste to be extracted is filled into the barrel to one-third its height; the valve on the steam-pipe is opened and steam sent in, until the leather, which is stirred two or three times during the fifteen minutes' passage of the steam, is heated, which may be recognized by its dark brown colour. During the boiling the fatty matter contained in the leather becomes free, and appears on the surface of the separate pieces, whilst the condensed water collects between the two bottoms, whence it may be run off when necessary by an outflow tap.

After this treatment the leather is at once shovelled out of the barrel and put in layers of 3-4 cm. (1.2-1.6 in.) into press cloths of equal size. The press cloths containing the leather are now laid in piles in a vertical press (the plates of which have been warmed), in such a manner that upon each layer of waste comes a metal plate, and that there may be ten or more such layers, according to the press, above one another. As the press-plate attached to the ram descends the fat is pressed out of the leather waste; it flows away until it becomes thick by cooling, which may be prevented by arranging under the bottom plate of the press a jacketed space permanently heated by steam. As soon as the fat ceases to flow away, the ram is screwed back, the cakes removed from the press, the cloths removed, and the naked cakes set out to dry. The fat obtained by pressing, which is absolutely pure, and has not in any way suffered by the action of chemicals, may at once again be used for stuffing hides and skins. As a matter of fact, it is better than the fresh fat prepared from tallow, dégras, and cod oil, since any resinous constituents or other injurious substances have been removed by the above process. The dried press-cakes are subsequently ground, producing an excellent fertilizer, which can be used without any other addition, and finds a ready sale in the market.

In the preparation of chamois leather a considerable

amount of cod and whale oils is pressed into the leather; part of this combines with or is closely held by the fibre, but a considerable proportion is pressed out again or removed by scraping with a blunt instrument and subsequent treatment with alkalies, which forms an emulsion, from which the oil is recovered by the addition of an acid. This is the English and German method of treatment, the product being known as "sod" oil. In France the skins are fermented for a short time, then thrown into warm water and pressed in a hydraulic press yielding a larger proportion of oil which is of a higher quality and is known as *möellon* or *dégras*. These oils are largely employed by curriers for stuffing leather, for which purpose they seem eminently fitted. During the treatment the oils undergo a remarkable change, their chemical constants being considerably altered.¹

¹Lewkowitsch, "Oils, Fats, and Waxes".

CHAPTER V.

LEATHER WASTE.

LEATHER cuttings are made into artificial leather, which can be used for the welts and heels of boots. The manufacture is very simple (according to the "Deutsche Ind.-Zeit."). The leather waste is, with the addition of a binding medium, made into rectangular plates, which are put one upon the other, pressed in a hydraulic press, dried, and rolled. It is at once evident that this leather is only suitable for cheap work, and cannot be used where it is exposed to the action of water.

The process of Sören Sörensen, of Copenhagen, is as follows: If the leather waste is impure, it is first freed from all foreign constituents, after which it is converted into a uniform fibrous material in a machine constructed for the purpose. When this finely divided leather is mixed with ammonia solution, a gelatinous mass is formed, which, when pressed into moulds or rolled into sheets and dried, gives a very hard and stiff material of considerable cohesion, but without elasticity, and soluble in water. In order to make it elastic and resist the action of water, it is mixed with india-rubber. The rubber, the quality of which is not important, as finest Para or the commonest African qualities can be used, is squeezed and washed in the washing-machine, which consists of two grooved steel rollers, over which is led a stream of water, which has the double effect of washing the rubber clean and preventing it from being burnt by the heat generated by the friction. After washing, the rubber is dried, cut up, and dissolved by means of benzene, carbon bisulphide, or other suitable solvent. The quantity of rubber to be dis-

solved varies according to its quality. Para rubber is dissolved, or rather gradually swollen, by 4 parts of solvent; Central American scraps require 3.5 parts, Guayaquil rubber 3 parts, and African rubber 2.5 parts. The rubber so prepared is then mixed with the leather and ammonia and the mixture well stirred. The proportions of the mixture depend on the quality of the product to be made. For example, for soles, 25 parts of solid rubber, 67 parts of ammonia, and 67 parts of leather; for heels, 25 parts of rubber, 80 parts of ammonia, and 80 parts of leather; for welts, 25 parts of rubber, 75 parts of ammonia, and 90 parts of leather. After kneading until the mass is quite homogeneous, it is dried. During the drying it is subjected to progressive pressings, the intensity of which varies according to the destined application of the product. For sole leather the greatest pressure is used—about 450 kilos per sq. cm. (about 2½ tons per sq. in.). After pressing, the substance is either painted or lacquered, or treated in some other way to give it a similar appearance to natural leather.

✓Smith and Johnson, of Huntington, dissolve the waste leather in sulphuric acid, pyroligneous acid, and fusel oil, then add melted wax, and mix the whole intimately with paper pulp, which has also been previously impregnated with wax. The mixture is then dried, ground, steamed, and pressed in the desired moulds. Such leather is said to be waterproof and very durable.

The leather made by the following process, published in Ackermann's "Gew.-Zeit.," is as pliable and durable as ordinary leather of the same thickness, may be used for the same purposes, and is equally waterproof. The mixture consists of 1 lb. of india-rubber to 3¼ lb. of leather waste of any kind in the form of raspings. In order to mix these substances intimately, the rubber is dissolved in benzene or carbon bisulphide; when dissolved, 1 lb. of ammonia is added and the mixture well stirred. The rubber is then precipitated with a greyish-white colour; the leather waste is next gradually kneaded into this pasty mass. When the mixture is

homogeneous, the stiff paste is rolled or pressed into sheets, cords, pipes, rings for making cold-water pumps tight, flanges, and valves. The product is better than vulcanized rubber or leather alone.

R. Jäkel, of Berlin, has patented *a machine for producing so-called artificial leather*. In Fig. 8, *A* and *B* are two smooth drums; *C*, *D*, and *E*, three smooth massive rollers. The bearings of the drum *B*, and of the rollers *C*, *D*, and *E*, can be fixed by screws in any position. *A* and *B*, also *C* and *D*, rotate in their bearings, whilst *E* is fixed. The pattern is stretched round *A*, *B*, *C*, *E*, and the ends stitched together.

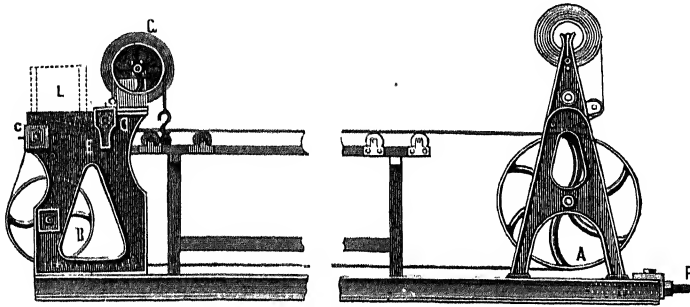


FIG. 8.

The machine is driven from the drum *A*, which moves both the pattern and the system of rollers.

G is a roller, upon which is wound the backing; its spindle rests at one side in an open bearing, and at the other in a hole, so that it can readily be changed. A brake acting on the projecting spindle keeps the fabric stretched, and ensures a regular feed. *L* is a sheet-iron pan with double walls, through which hot water circulates in order to keep the mass in the pan hot; its width is equal to that of the machine. The mass flows out of the pan *L* on to the pattern, where it is distributed by a movable guide towards the sides, and is then spread on in the desired thickness by means of the rollers *D* and *E*, or, rather, by passing between *D*, which is covered by the backing, and the pattern; at the same time the mass receives the design from the pattern. The mass

cools on its way to the drum *A*, when it is finished; it is then wound on the roller *N*, which is turned by a handle, *O*.

In order to obtain the negative, or pattern, of a material, such as leather, damask, etc., the original is drawn round the system *A*, *B*, *C*, *E*, in the same manner as the pattern in the manufacture, and kept stretched by means of the screw *F*. The original is then lightly coated with oil, so that the mass may subsequently easily be removed. In the pan *L* is the mixture for the pattern, consisting of glue, glycerine, and pyroligneous acid. The mass is applied in the same manner as described above. The surface is then hardened by treatment with acetate of iron, and sufficiently dried.

The mixture for the manufacture described above consists of glue, colour, glycerine, linseed oil, soap, gallotannic acid, and chromic acid.

ARTIFICIAL IVORY.

✓Leather waste may also be used in the *manufacture of artificial inlaid ivory*, which is said to be obtained from the bones of goats and sheep and pale or buckskin leather. The bones are treated with bleaching powder for ten to fourteen days, then washed in clean water and dried. When this is done, the bones and the leather waste are dissolved together in a pan with steam, so that a uniform fluid mass is obtained. To 10 lb. of this mass $\frac{1}{4}$ lb. of alum is added, and when this is well mixed the scum which has risen to the surface is skimmed off, until the mass is quite clear and pure, then whilst still lukewarm the necessary colours are added, the mixture strained through a clean linen cloth, and poured into the requisite moulds. When sufficiently cooled the cast mass is removed from the mould and laid on linen stretched over a frame, upon which it dries in the air. When quite dry it is soaked in a cold solution of alum for eight to ten hours, until it has attained the required hardness; 1 lb. of alum is used to 2 lb. of inlay for this purpose. When taken out of the alum solution the inlay is washed with fresh water, and again dried on the frame mentioned before.)

Leather Waste for the Manufacture of Glue.—In regard to the application of waste leather in making glue, J. Repp has constructed a machine for disintegrating the leather. It consists of a cast-iron box 3 metres (9 ft. 10 in.) long and 1 metre wide (3 ft. 3 in.), with rounded angles. The box is divided by a sheet-iron partition 5 mm. thick ($\frac{1}{8}$ in.) into two parts, which are connected at the round sides by the water which circulates through. At one end the water enters under the supply pressure, it passes through one division, and then back through the other to the outflow. The box is made in two pieces, at the top is a horizontal shaft with a roller studded with knives. The middle of the shaft is 640 mm. (2 ft.) from the bottom, the roller is 650 mm. (2 ft. 2 in.) in diameter; the height of the box is 1000 mm. (3 ft. 3 in.); it is provided with strengthening ribs. The knife cylinder consists of a drum in which is screwed a knife projecting 42 mm. ($1\frac{1}{2}$ in.); below it is brought a long knife, which can be adjusted at greater or less heights, according to the treatment required. The roller is driven by a belt at a speed of 120 revolutions per minute, thus the water and the leather which is being washed in it circulate through the roller, where the leather is cut to pieces. A charge of leather is 200, 150, or 120 kilos (4 cwt., 3 cwt., or $2\frac{1}{2}$ cwt.), according to the size and speed of the apparatus. In setting the machine in motion the box is almost filled with water, for which purpose it is connected with a pump or water supply. The working side, in which are the roller and the arrangements beneath, is somewhat wider, thus the leather stands at a rather higher level on the other side, in consequence of which it approaches with a certain velocity, due to the difference in level. The throat consists of a cast-iron frame with a wooden lining, upon which the long knives are fixed and screwed. This throat at its upper concave part occupies almost one-quarter of the circumference of the roller, with which it is concentric; it falls away at both sides in an inclined surface of iron or wood. The cooled leather is well divided in this simple apparatus, which requires little attention; at the same time it is washed

clean, so that it may at once be used in glue-making. The apparatus works excellently, since the leather is better purified and divided by the constant flow of clean water than by the older methods, in which the leather was first hung in the water in large baskets on a chain and then was ground after again drying. This apparatus is termed a hollander, but is not to be confused with the hollanders of paper-works.

Leather which has been tanned with a substance insoluble in water, such as chamois or bark-tanned leather, is not at once suitable for glue-making; it requires a complicated treatment, which, however, is always profitable. In the case of bark-tanned leather, the manufacturer has to make sure that all the tannic acid is removed from the animal tissue, since only a small quantity of this substance is sufficient to remove from the tissue its property of dissolving in water, and thus of producing glue.

In the first place, it is important that the leather waste should be converted into the finest state of division, for which a half-stuff hollander, such as is used in pasteboard and paper-works, is the most suitable.¹ The advantage is that the leather is not only disintegrated and washed in a manner which renders it very suitable for glue-making, but it can also be used in the manufacture of leather book-covers, which are very soft and of good appearance when made from leather stuff mixed with rag or wood pulp.

When the leather waste has been so prepared, and, in particular, well washed, it is chemically treated. Stenhouse uses a boiler working at two atmospheres pressure, and adds 15 per cent of lime to the leather mass to be treated, the lime being suspended in much water. Others use caustic soda of 1.025 specific gravity to extract the tannin boiled with this leather paste for twelve hours. After boiling, the water is run off, the paste pressed, and again boiled with caustic soda of the same strength. The soda is now carefully washed out, which is done in the hollander. If the caustic soda in the

¹ F. Dawidowsky, "Die Leim- und Gelatine-Fabrikation," Vienna.

liquor first drawn off is neutralized, the solution can be used for tanning or as tannic acid for other purposes.

The following is another process: 1.5 lb. of oxalic acid is dissolved in 12 litres (21 pints) of water, the boiling solution poured over 50 kilos (1 cwt.) of leather waste, and the mixture kept in the water-bath at a temperature of 80-100° C. The leather should then dissolve; when this is the case, 15 litres (26 pints) of water are gradually added until a uniform mass results. The paste obtained by slaking 5 lb. of quicklime is then added, and the whole well mixed, when the mass becomes friable and powdery. It is now rubbed through a wire sieve and the still moist mass exposed to the air. After three to four weeks the tannic acid is destroyed and the mass becomes lighter. The lime is removed by means of water and hydrochloric acid. If all the tannic acid should not be destroyed by the exposure to air, in boiling out the crude glue, 0.5 kilo (1.1 lb.) of ammonia and 0.5 kilo of ground pyrolusite is added to 50 kilos (1 cwt.) of the leather. Frequent turning over and gentle heat during the exposure to air hasten the process of decomposing the tannic acid.

As a final resort the leather waste is ground and used as a manure, for which purpose, though it contains a high proportion of nitrogen, it is not eminently fitted, owing to the fact that the nitrogenous matter has been rendered insoluble by the tannin, and its decomposition is extremely slow.

H. P. D. Lissagaray has obtained a patent for a new process for manufacturing an assimilable *fertilizer from leather waste*. The waste is immersed for about 5 minutes in water to which has been added about 10 per cent of strong sulphuric acid, or a sulphate such as alum or manganese sulphate. It is then dried in the open air, and finally in a current of hot gases. The material has now become quite friable; it is ground in a suitable mill to a fine flour, which is readily accomplished.

CHAPTER VI.

FUR AND FEATHER WASTE.

Utilization of Furriers' Waste.—Furriers produce a quantity of waste, which can only partially be employed, by neat and careful joining, to produce fur articles. A large proportion of the smallest cuttings constitutes valuable material for the hatmaker. No furrier, when cutting, should neglect to have at his side a small basket, into which the clippings can be thrown; otherwise, after first being dirtied on the floor, they have to be sorted out from other cuttings of all kinds. The waste pieces may be utilized as described below.

The waste grey pieces of monkey fur are used to fill the star-shaped and round mosaic fur covers of opera-baskets.

The feet and heads of astrachan, carefully fitted together, afford a material for covering gloves and hunting-mittens.

Pieces of bear-skin of all kinds are in great demand by brushmakers.

Cuttings of beaver and musk, even the smallest, are sought after by hatmakers at a good price. The forehead pieces of beaver-skins, placed together with the hairy side outwards, may be well used as trimmings on furs; larger pieces are very suitable for caps. The heads of musk, with the eyes and ears taken out by two cuts going from the eye over the ear, cut into triangular shape and joined together star-wise, may be used for linings, as also may the short ends.

Long-haired pieces of badger, such, for example, as are cut out of the middle in making covers for knapsacks, are highly prized by brushmakers.

Fox: the tails are used in making boas, and are also the most valuable material for ornamenting opera-baskets, foot-warmers, gloves, etc.

Goose and swan : the feathers are plucked from the waste pieces and used for stuffing muffs. Powder-puffs may be made from larger pieces.

Grebe : wings joined to heads, or half small wings, make handsome ornaments for bonnets of seal and rabbit-skin, or of seal and musk.

Considerable quantities of waste feathers of all kinds are used for stuffing mattresses, cushions, etc.

Hare : the ears of hares are frequently set together, i.e. stitched near together on linen, and used in making hunting-mittens and caps. The process is, however, not to be recommended. The hatmaker takes all the rest, with the exception of the black pieces, which may occasionally be sold to toy-makers.

Ermine scraps are frequently bought in order to make imitation tips ; but this is only done when the pieces are fine and of good size, and ermine skins are very dear.

Polecat : the scraps are bought by the Greeks to make linings ; the heads, when preserved, on account of the expression, are used for ornamenting hunting-muffs ; also, when cut into triangular pieces, for the mosaic covers of opera-baskets. The tails are used in brushmaking.

Rabbit-skins : the heads of large skins are put together to make wristbands, those of small skins for trimmings. Large sides may often be put together to make collars. All the rest, with the exception of the black portions, is used by the hatmakers. Enormous quantities of rabbit-skins are now converted into furs in imitation of the skins of other animals.

Cat-skins produce little waste. Good cat-skins when damaged may be used as tips in white rabbit muffs. Tails are practically of no value.

Lynx : the feet may be made into cheap trimmings. There is practically no other waste.

Marten : the foreheads may be used for the mosaic covers of opera-baskets, as also the throats, which may be used together with the feet for linings similar to sable, but heavier.

The tails are used for decorating ornaments, and also in brushmaking.

Mink : the cuttings are put together by the Greeks ; the tails, like those of the marten, are used for ornamenting ladies' trimmings, and for borders. The foreheads are also used for making the fur covers of opera-baskets.

Otter : fine material for hatmaking, but generally put together by the furrier, cleaned or dyed. The tails, when put together, form handsome and durable hunting-muffs.

Sea-otter : good pieces are highly prized ; in Russia they are principally joined together for cap-linings.

Sheep-skins : large pieces are joined together for lining opera-baskets.

Raccoon : the hairy sides are joined together for sleeves, or even for fur linings ; the heads are used for trimmings on black fur with raccoon borders ; the tails give durable trimmings.

Sealskin pieces are valuable. In England the smallest are joined together for caps, etc.

Skunk : the tails are bought by brushmakers. The white and black foreheads, properly joined together, and often worked in with triangular pieces of black cat-skin, make very handsome trimmings, especially for fox-skin.

Goat-skin waste is bought by brushmakers.

Hair of all kinds can be utilized. Cow hair is employed as a binder for plaster in building. Camel's hair is now used for the manufacture of special clothing for cold climates. Pigs' bristles are used for the manufacture of the best kind of brushes, for which purpose they are distinctly valuable.

The Waste of Tanned Sheep and Lamb-skins, as produced in the clothing industry, is mainly utilized by shaving off the wool, which is used in cloth-making, whilst the leather is bought by makers of prussiate of potash, hide-glue, and artificial manures. Gawalowski has discovered a method which makes it possible not only to separate the wool from the leather in its original length and without loss of strength for spinning and textile purposes, but also, when possible, to obtain the leather in a commercially useful form.

If the skins are immersed in a moderately strong solution of caustic potash or soda, the wool hairs are in a short time entirely dissolved, and there remains a bare, slippery hide, which, after being well washed with water, forms an excellent raw material for the manufacture of prussiate of potash or glue. Since the wool is entirely dissolved in the alkaline solution, the latter can be used for the preparation of ammonia, and especially for "animalizing" vegetable fabrics, so that they may dye more rapidly. This process may be applied in the manufacture of jute carpets, and in weaving jute tapestries and hangings.

If the skins are immersed in strong ammonia, the leather is attacked in such a manner that, on taking out after an immersion of some duration and drying, first in the air, then at 30-40° C., it is now in the form of somewhat friable pieces of skin. It is therefore only necessary to bring the wool into a tearing or beating machine, and next to card it, in order to obtain, on the one hand, the wool entirely as a good textile material, and, on the other hand, the leather waste in the form of a hide which can be dried and ground, and like meat meal and bone meal is an excellent fertilizer.

If the skins are immersed in a moderately strong solution of an alkaline carbonate—of soda or potash—the hide swells considerably in time and the hair may then be more completely separated by suitable apparatus from the pliable skin, so that on the one hand it results in a leather waste as in the first method, and, on the other, wool exactly as in the second method. This process, accordingly, combines the advantages of both the preceding methods, is the most simple and most lucrative, and also, up to the stage of the mechanical separation of the wool, the cheapest. Prussiate of potash works, which work up "dry liquor" into black potash, may combine this minor industry with their main process in a rational and lucrative manner, since the leather is an excellent material for adding to the melt, and their black potash is already obtained containing nitrogen. The saleable wool will then produce a not inconsiderable profit.

CHAPTER VII.

WASTE HORN.

Utilization of Turnings and Filings.—The waste materials are mixed with a saturated solution of potash and lime, by which the horn substance is attacked and finally transformed into the condition of a jelly, in which state, by the application of a gentle heat, it may be cast into moulds and pressed, when the mass loses moisture and becomes hard and coherent. A final pressing, under the influence of heat, gives the moulded mass its finished form ; it may then be worked up into the most varied articles—pipes, cigarette-holders, stick handles, buttons, etc.

Horn waste may also be utilized in the following manner : The turnings, raspings, and filings are moistened and pressed into a cylindrical metal mould by a metal piston to a solid cake, heat being applied. The mass is then rasped to a fine powder, which is again pressed in the same manner ; the operation is repeated until the mass has acquired a sufficient degree of hardness and solidity. Finally, it is again rasped and carefully sieved, so that all the coarser particles are removed. As a rule, horn and tortoise-shell waste are worked up together ; the articles are then less brittle than when made from tortoise-shell alone. From the fine powder the finished substance is obtained as follows : The powder is brought in layers between brass plates ; several such layers are placed under the press, and this brought into boiling water, when the mass becomes hard and coherent. The plates are then further worked. Finished objects may also be pressed out of this mass if the necessary moulds are provided.

Horn filings may be brought by the following process into such a condition that, from the mass, stick and umbrella handles and many other articles may be made by casting in

moulds. One kilo of quicklime, 500 grms. of potash, 40 grms. of tartar, and 30 grms. of common salt are dissolved in water, and then one-third of the quantity of water evaporated off. The rasped horn or turnings is then thrown in and boiled, until the mass becomes so thick that it can be poured into a mould, which must be well oiled, whether it be of metal, wood, or earthenware. If it is desired to colour the horn, the necessary colour is stirred into the fluid mass before casting.

The waste horn may also be boiled in a strong lye of potash and lime, until the mixture is thick enough to be poured out and moulded; before casting, a colouring addition may be given.

In order to obtain solid horn from waste, Pathe lays it for an hour in a liquid consisting of a cold saturated solution of boric acid in water, and a cold saturated solution of arsenious acid in dilute hydrochloric acid, the quantity of boric acid being twice that of the arsenious acid. The vessel containing the horn substance, swollen by this treatment, is then placed for an hour in a water-bath at about 60° C. Finally, the horn substance is subjected to considerable pressure by means of a piston in a closed iron mould, heated to 120° C., until all the liquid is removed. After cooling, the pressed mass forms solid plates of horn, which can be worked like natural horn, and are characterized by pliability and elasticity.

WASTE HORN IN THE MANUFACTURE OF FERROCYANIDES.

At one time a considerable quantity of waste horn, hoofs, leather, etc., was used in the manufacture of ferrocyanides, but this is now made from the "spent" oxide of gasworks far more cheaply.

Horn Piths in the Manufacture of Glue.—The piths of bullock's horns, when boiled as previously described, form an excellent strong size, which is used very largely in carpet manufacture and for other purposes under the name of pith size.

CHAPTER VIII.

FISH WASTE.

Utilization of Fish Scales.—In the year 1874 a method was discovered by which fish scales might be used in the production of ornaments, artificial flowers, inlaid work, and the like. Layers of fish scales, bound together by any binding medium, are now better replaced by mica waste, which is more easily coloured and applied. E. and J. Huebner, of Newark, in 1874, obtained a patent for the following process: The fish scales are cleaned in a suitable manner until they appear transparent and horny. The large scales of fresh fish are the most suitable; old scales are useless, since they have lost their elasticity and transparency. In the process of Huebner the fresh scales are first treated for 24 hours with clean salt water, in order to loosen and remove partially the upper layers. They are then washed in distilled or clean rain-water, which is renewed every 2-3 hours. This is done five or six times. The scales are then separately and carefully rubbed with a fine linen cloth, gently squeezed in a press to remove moisture, and finally are laid for an hour in spirit, and again, as before, rubbed and pressed until dry. They have now the appearance of mother-of-pearl, and are very elastic and durable. They may either be used without further treatment or may be coloured as required.

Fish scales are used to prepare "pearl essence," or "fish-scale essence". The dace (*Leuciscus vulgaris*), one of the commonest fish in our waters, is washed with water to remove any adherent dirt, and then skilfully scaled, care being taken to remove scales alone, and not contaminate them with pieces of skin or blood. The scales are carefully collected and kept in a vessel of water, until a sufficient number for the

further treatment has been obtained. It is necessary to remove the scales from almost 40,000 dace in order to obtain sufficient to prepare 1 kilo of pearl essence, which quantity is, however, sufficient to make many thousands of artificial pearls. The vessel in which the scales are collected is best placed in an airy loft, since the scales very soon decompose and then give off a most unpleasant odour. In order to avoid this inconvenience the following process is adopted: The scales are covered, not with water, but with a solution of salicylic acid obtained by dissolving 3 grms. of the acid in 1 litre of water (3 in 1000). The salicylic acid is tied up in a little linen bag, which is suspended in the water, so that the acid gradually dissolves. By using this simple precaution the collecting vessel for the scales may be allowed to stand in the summer without the least injury. When a sufficient quantity of scales has been collected, the liquid above them is allowed to run off, and a portion of the mass of scales transferred to a large porcelain mortar, in which they are ground for a long time with a flat pestle. In consequence of the grinding, those particles are removed from the scales which are the cause of their silvery appearance. After long rubbing, the mass in the mortar is mixed with water, and the whole poured upon a closely woven linen cloth stretched over a tub.

The colouring matter of the scales, which is suspended in the water in the finest state of division, penetrates the cloth together with the water. The scales are again ground and mixed with water, when a second quantity of the colouring matter is obtained. After the latter is entirely collected in the tub the liquid is well stirred up, left at rest for some time, and then drawn off into glass bottles, in which it is allowed to stand until the colouring matter has completely settled to the bottom. The coarser portion of the colouring matter remaining in the tub is again stirred up with water and allowed to settle.

The water above the colouring matter is carefully poured off, and the latter finally collected in one bottle. In the moist state it has a silver-white colour and considerable

lustre; on drying, a soft silver-grey powder is obtained. This "fish-scale essence" can be kept for a long time unaltered under a solution of salicylic acid.

The mass with which the pearls are filled is prepared in the following manner: Completely colourless gelatine is swollen in an aqueous solution of salicylic acid: the liquid is then poured off, and the gelatine melted to a clear liquid by cautious heating in a porcelain dish. The fish-scale essence is now introduced and most intimately mixed with the gelatine. No definite figures can be given for the quantities of gelatine solution and fish-scale essence; the rule is to take no more of the latter than is absolutely necessary, because it is a costly substance. Thus no more of the "essence" is taken than is sufficient to cover the mass after it is introduced into the glass pearl.

The mixture is kept melted on a water-bath, and introduced into the glass pearls by sucking it up into a glass tube drawn out to a point, allowing a drop to fall inside the glass pearl, and turning the latter until the inner surface appears to be quite covered by the pearl essence.

In order to prevent the solidified mass from becoming detached from the glass wall, and to give the pearls a greater weight, they are filled with melted wax or a mixture of wax and paraffin. Pear-shaped pearls, which have only one opening, are filled with wax, and the opening closed by a small drop of melted pearl essence.

J. Loreau, at his works at Kernevel, near L'Orient, uses fish in the preparation of sardines in oil. A large quantity of waste is produced, consisting of heads, bones, entrails, bloody salt liquors, etc. This waste is collected, drained, heated in a pan and pressed; the cakes are dried and ground, when a fertilizer is produced. If treated with sulphuric acid, this fish guano would be very suitable for beetroot.¹

Substitute for Isinglass, also Gelatine and Glue from Fishes and Fish Waste.—A substitute for isinglass, also for gelatine and glue, is prepared by C. A. Sahlström of Stock-

¹ "Bull. Soc. Encouragement," 1877; "Dingler's Journ.," 227, p. 511.

holm, according to his patent, from fish and fish waste, by treatment with bleaching powder, potassium permanganate, and nitrous and sulphurous gases.

For this purpose the fishes, or portions of fishes, are first well washed in fresh water, and then left for from three to four hours in a solution of about 85 grms. of bleaching powder in 25-30 litres of water (1 in 300 to 1 in 350). After washing, they are treated with a solution of about 5 grms. of potassium permanganate in 25-30 litres of water (1 in 5000-6000), and then exposed to the action of the nitrous gases produced by heating 300-400 grms. of nitric acid for every 40 kilos of raw material (about 1 per cent). This gas may be first absorbed by water, or sulphur dioxide may be used instead of nitrous gases; the former would be obtained by burning about 200 grms. of sulphur for every 40 kilos of raw material (about 0.5 per cent).

The material, after this treatment, is washed; those portions intended for the production of the isinglass substitute are freed from their outer skins and dried and pressed at a gentle heat. The portions destined to produce gelatine or glue are, on the contrary, exposed to a temperature of 40-50° C. for from ten to twelve hours, by which the material is mainly dissolved. The mass is then forced through a strainer or sieve, allowed to stand for some hours, and finally dried, as is usual in the manufacture of glue or gelatine.

A considerable amount of fish scrap is produced during the extraction of the various fish oils. This is dried and converted into fertilizers. In the Menhaden industry the fish scrap from the presses falls into the buckets of a conveyor from which it is delivered to the drying room. 100 lb. of the mass from the cookers contains 22 lb. of dry matter and 78 lb. of water. In the press 56 lb. of oil and water are removed, leaving a mass of 44 lb. consisting of 22 lb. of dry matter and 22 lb. of water. The hot air drier for drying the fish scrap is almost universally employed. This consists of an insulated iron cylinder about 6 ft. diameter and 30 or 40 ft. long. It is provided inside with a series of iron flanges

or shelves, about 8 ins. wide, running the whole length. These are for the purpose of lifting the scrap and dropping it through the hot air. The cylinder is rotated by an electric motor, a forced draught of hot air being induced in it by means of a fan. The wet fish scrap is charged in at one end, while the dry scrap falls out of the other into a brick chamber, from which elevators convey it to the bagging room. The transit of the material through the drier occupies from 3-20 minutes, by which time the moisture is reduced to 7 per cent. A million fish will yield 75-85 tons of dry scrap.

Dry fish scrap is known as fish guano and is of considerable value as a fertilizer. The following are analyses of these manures as well as that of raw fish offal:—¹

	Raw Fish		Fish Guanos.	
	Offal.	Anchovy.	Herring.	Cod.
Moisture	50·58	8·06	6·14	6·24
Oil	15·51	—	—	—
* Nitrogenous organic matter	18·54	66·18	70·18	57·68
Alkaline salts	10·93	4·54	1·56	2·12
Phosphates	3·84	14·92	7·92	26·17
Carbonate of lime	0·48	3·28	3·68	6·35
Silica	0·12	3·02	10·52	1·44
	<u>100·00</u>	<u>100·00</u>	<u>100·00</u>	<u>100·00</u>
* Nitrogen equal to ammonia	3·31	8·62	10·42	10·13

Fish Meal.—Quite a considerable quantity of offals is produced in dressing and boning fish, heads, tails, skins, entrails, and bones; this is usually carted away to the destructor, but where it can be quickly applied to land it forms an exceptionally good fertilizer.

A new industry has, however, been developed in which these offals and also any fish which cannot be disposed of is dried in a current of hot air; it is then ground to powder in a disintegrator and is sold as "fish meal".

This fish meal has been found to be a very valuable food for cattle. It was first made in Norway; subsequently the manufacture was taken up in this country, but the farmers were at first extremely reluctant to give it a trial so that large

¹ Ivison Macadam, "Journ. Soc. Chem. Indt.," 1888, p. 83.

quantities were shipped to Germany. Now that the price of feeding-stuffs is so extremely high more attention is being given to this material, and no doubt in a short time all that is made here will find a ready market amongst the farmers. Fish meal contains about 55 per cent of albuminoids, therefore it is an extremely concentrated food. It should, of course, not be fed to cattle alone, but should be judiciously mixed with other materials such as oilcake or grain.

CHAPTER IX.

MOTHER-OF-PEARL WASTE.

Utilization of the Waste of Button-making.—A substance which formerly could not be utilized, is the lining cut out by button-makers from the shells, the innermost layer of which is the so-called "mother-of-pearl". The suggestion was made to convert this waste into a fine powder, when a soft bronze powder, of a silky, metallic lustre, was obtained, which could be employed in many ways, especially since it can be coloured to any shade. The pulverization of the mother-of-pearl waste is accomplished in the same manner as that of wood which is to be worked up into wood-pulp, i.e. the waste is ground by a suitable rotating grindstone, in such a manner that it is first beaten to pieces and then brought into a cylinder, in which it is pressed on the grindstone by means of a piston. The powdered mother-of-pearl obtained in this manner is then levigated, and, after drying, brought on the market, with or without previous dyeing. In order to convert mother-of-pearl into a glittering powder, suitable for makers of artificial flowers, the shells are first treated in closed vessels with high-pressure steam, after which they can readily be powdered. The use of this powder in making wall-papers is said to be profitable: 1 sq. metre of the paper requires 3.5 grms.; thus, a roll of paper 9.5 × 0.5 metre (31 ft. × 20 in.) would require about 14 grms. ($\frac{1}{2}$ oz.) of powdered mother-of-pearl, the cost of which would be 1 pfennig per gm., or 10 marks per kilo (4s. 5d. per lb.). The chemical works of M. Hess, at Neufünthaus, Vienna, produce "pearl silver" from such waste.

CHAPTER X.

VEGETABLE IVORY WASTE.

Utilization of the Waste of Ivory-nuts.—Guild, of New York, makes moulded objects of all kinds, especially buttons, from the waste of ivory-nuts. The process is as follows: The waste is ground to a fine powder and the mineral particles removed by stirring up the powder with much water, when the mineral constituents rapidly sink to the bottom, whilst particles derived from the nuts remain suspended. The water is then drawn off together with the suspended powder, which is separated by filtering and pressing, and then dried in any suitable manner. The dry powder is sieved and mixed with enough water to make the separate particles cohere. The process may also be simplified by drying the powder only to such an extent that it retains the proper quantity of water. The mass obtained is filled into moulds, which give the shape of the desired article, and pressed in a press whilst subjected to a temperature of 125-150° C. According to the size of the article the mould containing it is subjected to the action of pressure and heat for a period of 3-10 minutes. The pressed articles are then taken out of the moulds, dried, and finished. In making coloured articles, a colouring matter is added to the mass before it is filled into the moulds.

Brolík employs ivory-nut waste as a hardening material for Bessemer steel and iron. The hardening powder is made from the sawdust and the smaller turnings and filings. The larger pieces can be ground in a drug mill or other similar apparatus, yet it is advisable to employ instead a suitable rasping arrangement, since there is then a considerable saving

in cost—ten to twelve shillings per cwt. being charged for grinding the shavings. The powder obtained in this manner may also be mixed with other hardening agents. The latter substances can also, if they are soluble in water or at least able to impart their special properties to it, be made to penetrate the powdered portions of the nut, by placing the powdered nut, which strongly attracts water, in water containing the requisite substances, removing it after twenty-four hours, and thoroughly drying it. Hardening experiments were conducted in the following manner with unmixed ivory-nut powder, ground to the size of fine sand: A cementation box, filled in the ordinary manner with Bessemer steel plates and iron to be hardened, and with leather charcoal, received at the top at one narrow end a layer of the ivory-nut powder, in which were placed a disc about 5 cm. (2 in.) in diameter and then a piece of steel about 12 mm. ($\frac{1}{2}$ in.) thick. The lid was then placed on the box and the joints luted with clay. After heating in a coal fire for three hours the box was opened. When cold it was found that, in consequence of insufficient or irregular heating, insufficient time or bad leather charcoal, the iron placed in the latter was irregularly hard, so that it could not be used and had to be hardened again; whilst the two pieces in the ivory-nut powder were of uniform hardness and could not be attacked in any place by a good new file without blunting it. The disc was then broken; it showed on all sides a completely regular hardened crust about 1 mm. ($\frac{1}{64}$ in.) thick. The hardening experiment was then repeated with fresh ivory-nut powder; in regard to the hardness, exactly the same results were obtained. Although the hardness of the iron immersed in the ivory-nut was faultless and of a regularity not hitherto obtained, it was found that ivory-nut powder of too fine grain was not suitable for hardening steel which was required to be of good appearance. The surface of the hardened steel was covered with spots, which were presumably produced by the penetration of the exceptionally fine grains of powder into the pores of the iron when enlarged by heat, where they remained and were fixed

by the contraction during or after cooling. It is not impossible that with coarser powder, as from the sawdust and raspings, or by mixing or saturating the ivory-nut powder with other suitable ingredients, this hindrance to the general use may be avoided.

CHAPTER XI.

WASTE WOOD.

THE utilization of waste wood is worthy of attention for two reasons. In the first place, from a purely technical point of view, through the production of more or less valuable products from small and objectionable waste; in the second place, from the economic point of view, since nothing should be lost, and material once introduced in the manufacture must be worked up into new forms.

Perhaps, in a certain sense, necessity was the cause of the endeavours to utilize wood waste, as, for example, was also the case with blast-furnace slags, which, by their immense accumulations, diminished the working spaces of the works to such an extent that the removal of these by-products became a question of life and existence to the smelters.

It is true that there is nothing to hinder the technical utilization of waste wood, but, unfortunately, it is a hindrance that the waste is locally produced and must be utilized on the spot. Carriage of waste wood to any considerable distance renders its conversion into new products quite unprofitable.

In districts where waste wood is produced in large quantity and—what is equally important—regularly, its utilization is very profitable, especially when, by the development of special processes, products can be obtained which possess the natural good qualities of the wood, and also valuable qualities artificially added. On the ground of many years' experience, the author is strictly of the opinion that valuable imitations and complete substitutes can only be obtained by using the less valuable waste of the original substance. Imitations of,

and substitutes for, leather can practically only be obtained by suitable treatment of waste leather; imitations of, and substitutes for, wood can only be produced from wood waste.

The industries which produce imitations and substitutes should abide by this principle; they would then be spared many disappointments, and we should read fewer patent specifications, of which it can at once be said that they are practically worthless.

Waste wood may be utilized in a variety of ways, but it would be unjust to designate all as equally good. Neither in execution nor in profit are they of equal value.

In regard to the appliances employed in utilizing waste wood it appears to be very difficult to give any accurate and particular statement, since the manner of working and the products obtained are too varied. Generally speaking, it will be sufficient to say that the necessary appliances are similar to those used in producing plastic masses—mixing and kneading machines, moulds and presses.

If it be intended to consider seriously the manufacture of products from waste wood, it is first necessary to obtain clear ideas on certain points. The first question is always, Is there a certainty of a sufficient, reliable, and lasting supply of suitable waste wood? This question favourably answered, and the raw material thus secured in a sufficient and permanent supply, then comes the second question: Does the existing or main business possess any of the appliances or the necessary conditions for the manufacture of particular products from waste wood? This question appears very important; it affects the question of profit. The last question to be raised is, Does the article which is to be made meet an actual need, and do time and circumstances appear to favour an abundant sale of the article, so far as human estimates go, as the sum of the deliberations, comparisons, and experiences of the manufacturer and others?

These questions must first be drawn up, considered, and answered. The more thoroughly and practically they are

examined, and the more precisely the answers are drawn up, the more solid will be the foundation for the manufacture and the better prospects will the intended process have.

Special instructions for answering the first two questions cannot be given, because they are of a personal or local nature. Hints may be given in regard to the answer to the last question, which will render possible a rapid and practical survey and a course of action.

An important wood waste is *sawdust*, both on account of the quantity and frequency of its production. This is to-day utilized on a large scale. The most obvious and simplest method of use is as a fuel, for which it has often been proposed, but the first attempts were unsuccessful on account of the lack of suitable apparatus for burning. Now, however, these difficulties have been completely removed by a rational construction of furnaces and grates, which enable fuels in powder or dust to be employed without difficulty.

Another method of utilization, the first to touch on a real branch of manufacture, was to prepare *artificial wood from sawdust*, the binding medium used for the sawdust being glue solution and water-glass, also colophony, blood, and glue with potassium bichromate. The best binding medium for sawdust is glue, to which bichromate of potash is added in order to make the compound waterproof. On exposure to light, chrome glue, insoluble in water, is formed. The glue solution is prepared from five parts of good pale glue and one part of isinglass by softening, slow heating with water, and careful straining. The quantity of water is decided by the nature of the glue; it ought not to be too small, being such that the liquid does not form a jelly on cooling, but only just begins to set. Moulds of metal, gypsum, or sulphur, after thoroughly oiling—or even of wood, if previously varnished with a spirit shellac varnish,—may be used for shaping the wood mass mixed with glue. A thin layer of the mass may be first applied, pressed well into the mould with the fingers, then the remaining space filled with mass prepared from coarser sawdust, the surface covered by a large plate, and weighted.

Before taking out, which is easily done as soon as the mass is somewhat dry and coherent, the superfluous matter is cut off with a broad, thin knife, and the under surface of the relief thus made level. The articles can then be varnished or gilded, and treated just as ornaments cut out of wood.

The *wood paste* prepared by the method of Kletzinsky is very well worth attention: 160 parts of sawdust—best from soft woods—are well boiled in a solution of 100 parts of sulphate of alumina in the necessary quantity of water, and then allowed to cool; 50 parts of glue are dissolved at the boiling point in 100 parts of water. The glue solution is well mixed with the sawdust paste; the mixture is kneaded, rolled in press sheets, and pressed under a very powerful pressure. The pressed material, which is at first very brittle, on gradual drying in the air acquires a surprising degree of hardness. When sufficiently firm, it is moistened from three to five times with a dilute solution of potassium carbonate in water, after which it is finally dried. In this manner the separate particles of wood become united by a kind of alum-tanned glue, which is no longer soluble in water, and is of horny hardness. Any desired colouring matter may be added to the alumina mordant, and also ground dyewoods, in order to obtain coloured wood pastes. By adding coarse mixtures of wood meals of different colours beautiful mosaic plates for parquetry may be produced.

The property of sawdust to act as a non-conductor of heat has naturally been utilized. It has been recommended for lining ice safes, and is now used for this purpose. There is, however, no doubt that in this respect it leaves much to be desired, apart from the fact that a regular supply depends on local conditions, and that it is far from being the best for this purpose. (Cf. Infusorial Earth and Slag Wool.)

Sawdust is used for *burning black clay pipes*. A layer of sawdust and a layer of pipes, 300-500 in number, according to size, are placed in a large muffle. The muffle is then luted up, brought into the furnace, which is built up, with the exception of the firing doors. The sawdust is carbonized

by exposure to a red heat for 10-12 hours, and colours the pipes black. The pipes are next, in numbers of 20-50, placed on a round sieve with an equal number of holes, kept over a straw fire, when they become intensely black; they are finally polished by means of wax and a stiff brush.

Among the further processes in which wood waste is used is the *manufacture of oxalic acid*. In this case the operation is conducted on a large scale, and requires, besides some chemico-technical knowledge, also suitable appliances, so that it appears advisable to introduce this application of sawdust only where a suitable manufacture already exists, to which that of oxalic acid can conveniently be added. In view of the many applications of oxalic acid and its salts, there is no doubt of the demand.

The process is commenced by preparing the lyes. Potash and soda are mixed in such quantities that, after causticizing, the proportion of the potassium hydroxide to the sodium hydroxide may be as 40 : 60. The mixture of the two salts is dissolved in about eight times the quantity of water, and made caustic by boiling in an iron pan with slaked lime. After deposition of the calcium carbonate thus produced, the lye is drawn off into another iron pan, in which it is evaporated to a specific gravity of 1.3-1.4. The sawdust, which is to be used, must be freed from large pieces of wood by sieving; it is then mixed with such a quantity of the caustic lye that there are two parts by weight of alkali to one part of sawdust. Since it is important that the whole mass of the wood should be uniformly saturated by the alkali, the concentration of the latter is arranged so that, after thorough mixing, the whole of the liquid has been absorbed by the sawdust. The mass is then at once brought into the vessel in which the heating is to take place.

The yield of oxalic acid is the largest when the mass is spread out in thin layers; thus it is best to use for the heating very shallow dishes of about 2 metres (6 ft. 6 ins.) diameter, with rims about 5 cm. (2 ins.) high, in which the mass is spread out to a depth of $1\frac{1}{2}$ -2 cm. (0.6-0.8 in.). It is continu-

ously turned over by a stirrer, which at each revolution lifts the mass from the dish, and allows it to fall back.

It is of the greatest importance that the temperature of the whole mass should be brought to 240° C., but should not exceed this limit. It therefore appears to be advisable to heat the pans, not by direct fire, but by the hot gases drawn off from the fire. This condition is attained by connecting a fire-grate by flues with a low chamber, the roof of which is formed by the pans; in each flue is a damper, of careful construction, which renders it possible to regulate the admission of the fire gases or to cut them off altogether. By using an arrangement of this description, it is not difficult to keep the temperature of the mass within the desired limits. The sawdust, saturated with lye, is brought into the pan by means of flat shovels, by which it is spread out, the stirrer put in motion, and at the same time the pans heated by opening the dampers. At first only evaporation of water takes place, the mass gradually darkening until it becomes deep brown; at the same time a peculiar odour is perceived. When the temperature reaches about 180° C. the mass becomes paler again, finally acquiring a greenish-yellow colour. The temperature is now very gradually increased to 240° C., at which the mass is kept until particles of wood can no longer be seen when a sample is withdrawn. The dampers are then closed, the melted mass removed with flat shovels, and allowed to cool, or further treated whilst still hot.

In the latter case the melt is thrown into a pan containing hot water, in which it rapidly dissolves and heats the water almost to boiling. The heating is continued until the concentration of the liquor reaches 38° B., when it is run out into small crystallizing vessels, in which, during the rapid cooling, nearly all the sodium oxalate separates, this salt being only slightly soluble. Very little of this salt remains dissolved in the liquid, which contains potassium carbonate, caustic soda and potash, and humus compounds. In order to free the crystals of sodium oxalate from the mother liquor, they are brought into a tall tub with a false bottom, where

the mother liquor drains away, the remainder being then displaced by water. The mother liquors are evaporated to dryness, the residue freed from the humus compounds by roasting in the air, and the residual mixture of sodium and potassium carbonates again causticized.

In order that the soda united to the oxalic acid may again be immediately used in the form of caustic soda for the treatment of new quantities of wood, the sodium oxalate is treated in the following manner: It is dissolved in a very little boiling water in a vessel heated by steam, and then thin milk of lime run into the hot solution, which is kept in constant motion by means of a stirrer, until the decomposition is complete, i.e. until insoluble oxalate of lime and soluble caustic soda have been formed. The quantity of lime to be employed is calculated from the weight of sodium oxalate taken; since, however, both substances are not quite pure, the calculated quantity of lime does not agree with that really used. It is, however, important to bring no excess of lime into the precipitate, since otherwise in a later operation a larger quantity of sulphuric acid would be required than is needed to decompose the oxalate of lime. The precaution is therefore taken, after the greater part of the lime has been introduced, of taking repeated samples, which are filtered, acidified with acetic acid, and calcium chloride added; so long as a turbidity is produced, undecomposed sodium oxalate is still present.

The milky liquid is then run from the decomposing vessel into another, where it is allowed to settle, and the clear caustic soda solution drawn off from the precipitate. The latter is washed with water, and the first wash water, which still contains much caustic soda in solution, is added to the caustic solution; the further washings are, however, used to dissolve new quantities of the crude melt. The oxalate of lime, when sufficiently washed, is transferred to a tank lined with lead, stirred to a paste with water, and then with the calculated quantity of sulphuric acid previously diluted down to 15-20° B. The quantity of the sulphuric acid should be

equivalent to that of the lime used in the decomposition ; when two parts of sulphuric acid are used to one part of lime the sulphuric acid preponderates, and there is obtained a solution of oxalic acid containing free sulphuric acid. However, it is advisable to work in this manner, since the excess of acid accelerates the decomposition of the oxalate of lime, the sulphuric acid being utilized again in a later operation.

In order to hasten the decomposition of the oxalate of lime, steam is continuously introduced through a small lead pipe, which reaches to the bottom of the decomposing vessel. The solid compound is thus kept always suspended in the liquid ; the heating also assists the decomposition. After the addition of the whole of the sulphuric acid the liquid is allowed to rest, the solution of oxalic acid drawn off after the deposition of the gypsum, and the latter washed with water in a lead funnel lined with linen, the first washings being added to the oxalic acid solution ; the remainder are used in place of pure water to mix with the oxalate of lime in a fresh decomposition. The residual gypsum is an excellent fertilizer for clover, but may, since it is very pure, be dehydrated and utilized as plaster of Paris.

The solution of the oxalic acid is concentrated in a shallow lead pan, standing on a sand-bath, which is heated by an open fire, or better, by steam, until, in the summer, it is 15° B., in the winter, 10° B. It is then cooled to the ordinary temperature, when the dissolved gypsum separates in crystals. The liquid poured away from the gypsum is then further evaporated to 30° B., and set to crystallize in shallow lead vessels.

The mother liquors, separated from the crystals, contain the excess of sulphuric acid in addition to the oxalic acid ; the sulphuric acid is estimated, and the liquors added in the next decomposition of oxalate of lime, the amount of sulphuric acid added being decreased by the corresponding quantity.

The oxalic acid crystals are washed with cold water to remove adherent mother liquor, and are then purified by solution in boiling water and rapid cooling, so that only small

crystals may form. The compound is then sufficiently pure for commercial purposes; it contains a very small quantity of sulphuric acid and an equally small quantity of oxalate of soda or potash.

The manufacture of pyroligneous acid from sawdust may be applied in all cases where the production of acetic acid from alcohol is not profitable. One hundred kilos of sawdust give 45-54 litres of a liquid, which contains 4 per cent of acetic acid, and also 6-8 litres of tar.

The dry distillation of sawdust begins at a temperature of 100-130° C., at first only water coming over, the quantity of which naturally depends on the condition of the sawdust. According to whether it has been kept in the open or in closed rooms, it will contain a larger or smaller quantity of moisture, which influences the quantity of water distilling over, and also the consumption of fuel. It is therefore advisable, when possible, to give the sawdust a preliminary drying, before bringing it into the distilling apparatus. The temperature rises from 145-500° C.; the products of distillation are water, pyroligneous acid, wood spirit, and tar, also various gaseous substances, whilst charcoal remains. The acid products form the chief quantity when the temperature is rapidly raised; they must be rapidly removed if they are not to undergo a further decomposition.

In North America a very considerable amount of waste pine wood, twigs, chips, etc., is first distilled with superheated steam for the production of "wood" turpentine, and subsequently carbonized in the retorts for the production of wood alcohol, pyroligneous acid, wood tar, and charcoal.

New Source of Turpentine.—In view of the constant upward tendency of prices in turpentine any possibility of a fresh source of supply deserves the fullest investigation. A paper presented to the Newcastle section of the Society of Chemical Industry by Paterson and Forbester quotes some promising results obtained from what is at present a waste material, viz. the residue and waste cuttings from the very large quantity of pine woods used in the shipbuilding industry,

which at present is carted away and destroyed. The investigators set up an experimental plant for converting this waste material into a source of revenue by submitting it to fractional distillation. For this purpose they used an experimental still, consisting of a cylindrical iron retort 6 ft. long and 11 ins. in diameter, heated by hot air in such a manner that they could maintain it for any desired time at a constant temperature varying from 100-400 °C. This retort was connected with condensers and scrubbers for collecting and recovering the products of distillation. The various products obtained as the result of experiments, calculated on one ton of dried wood, are given as follows :-

	Pitch Pine.	Mixed Pine Woods.
Turpentine oil	14 gals.	8 gals.
Tar	97 "	49 "
Acetate of lime	30 lb.	50 lb.
Alcohol and acetone	1½ gals.	2 gals.
Charcoal	500 lb.	370 lb.

The authors state that the turpentine referred to in the above table is identical with American turpentine in all its properties, having a sweet pine-like odour quite free from any smell of creosote, and a specific gravity of 0.846. It may here be remarked in parenthesis that this gravity does not agree with the claim that the material is identical with American turpentine, the specific gravity of which is considerably higher than this, .867 being recognized as a normal figure. In fact, the product is obviously more of the nature of that produced in a somewhat similar manner in the United States under the name of "wood turpentine," and it is doubtful if, as the authors claim, it could compete on equal terms with genuine American turpentine, although there is not the slightest doubt that it would prove a valuable substitute. A further point of interest in this paper is the production of a large quantity of polymerizable oils which come off with the tar, and which, as the authors suggest, might

profitably be extracted and find extensive use as wood preservatives and in the preparation of priming paints.¹

In a certain sense *artificial vanillin* is a product obtained from waste matters. In the year 1861 T. Hartig found a crystalline substance in the cambial sap of the conifers, which he termed "laricin," but later, after he had ascertained its presence in the majority of coniferous trees, he named it "coniferin". It is obtained in the following manner: Pines, firs, larches, felled between the middle of May and the middle of July, are gradually stripped of their bark and bast layers; the young wood fibres, swollen with sap, are scraped off by means of pieces of glass from the hard woody layers, and collected in vessels beneath. The scraped-off material is at once separated from the sap by fine press cloths, and the sap immediately boiled. The coagulated albumin and the solid substances it encloses (cell nuclei, starch grains) remain behind on filtering through paper, whilst a clear filtrate is obtained, which, when carefully evaporated to about one-fifth of the original volume, separates the cambial sugar and also the coniferin in crystalline form. By treatment with cold water the difficultly soluble coniferin is separated from the sugar; it then crystallizes in white needles, generally united to form rosettes, which give a deep violet coloration with strong sulphuric acid.

Dr. Haarmann, of Holzminden, has given an account of the preparation of artificial vanillin in Post's "Zeits. für d. chem. Grossgew." The raw material for the preparation of artificial vanillin, says Haarmann, is coniferin, a glucoside contained in the cambial sap of coniferous trees. It is obtained in the districts where the trees are felled during the sap period—Thüringia, the Baden and Württemberg Black Forest. The coniferous—red and white firs—are barked, the sap lying below the bark, together with part of the bast, scraped off by means of a piece of glass or a knife, and collected in a vessel. The sap is filtered from the bast as rapidly as possible and boiled, since it readily ferments and completely decomposes. The liquid is then separated from

¹ "Oil and Colour Trades Journal."

the coagulated albumin, evaporated down to one-fifth its volume, and set aside to crystallize. After a short time the crystals produced are pressed to remove the mother liquor; 100 litres of the sap, which is very difficult to obtain, produce 0.5-1 kilo of coniferin. For the production of vanillin the coniferin is treated with oxidizing agents (sulphuric acid and potassium bichromate), and the vanillin either distilled in steam or extracted by ether. In order to separate the vanillic acid produced, the substance is subjected to purification by sodium bisulphite solution and then recrystallized. After this operation, vanillin forms an almost white crystalline powder, which melts at 80-81° C. Twenty grms. of vanillin are equivalent to 1 kilo of the best vanilla, since the latter contains on an average only 2 per cent of this compound.

The *application of sawdust as an addition to cement*, in order to prevent the formation of small cracks, is technically interesting. The sawdust is well dried, then sieved in an ordinary sieve so that only the small woolly flocks are used. The mortar is mixed from one part of cement, two parts of lime, two parts of sawdust, and three parts of sharp sand. The sawdust is first mixed dry with the cement and sand, and the lime then added.

Sawdust is also mixed with cementing agents such as magnesia and magnesium chloride, and laid on concrete floors with a trowel. It yields a durable and pliable coating which is very pleasing in appearance. It may be coloured by the addition of common mineral pigments, e.g. red oxide, ochre, umber, etc.

Wood waste finds another application in the *manufacture of casks*. The outer skin of the stems, removed when the tree is sawn up, is cut up by an ordinary circular saw into lengths equal to the length of the staves required. These lengths are now cut up into proper widths by means of a circular saw with two to three blades, which can rapidly and easily be put in motion. The wood is fed to the saw by means of rollers with deep grooves and running in elastic bearings. The pieces now come to a circular saw with a

vertical spindle and horizontal roller feed, by which they are cut to shape. The saw blade has a diameter of 23-24 ins. In the middle of the spindle above the table is a guide, to right and left of which, in front of the saw, and thus diagonally opposite, are grooved rollers in elastic bearings. By means of this arrangement two pieces can simultaneously be cut to different thicknesses. The staves now go to a trimming and slitting machine, in which they are cut into exact lengths and bevelled towards the inside, and the slits cut for the reception of the ends. This machine has a shaft upon which the slit-cutting tool runs, and two other shafts upon which run the circular saws which trim the staves. The saws and tools can be fixed at different distances apart to allow for varying lengths of the staves.

The staves are fed in by hand, each being laid with its hinder end against a guide, which can be moved backwards and forwards. The pieces of wood after this treatment come to the jointing machine, in which the staves are carried in a segment-shaped guide over a slit below which is a small stout circular saw. The staves receive in this machine an accurate joint, which make subsequent working by hand unnecessary, and enables the body of the cask to be at once built up. For the sake of easier carriage, which is important, the staves are tied up in a bundle. The ends of the casks are cut from smaller waste pieces in a similar manner to the staves. For this purpose wood is used which, by its structure, is unsuitable for staves. The separate pieces are pegged together, and finished on a machine which cuts out the round end. All the machinery may be tended by youths. With one set of machines several hundred casks can readily be made in a day. The sale of these casks, made from outer skins of trees and waste pieces, should be almost without limit; cement makers, millers, nail makers, and fruit dealers in particular buy them readily.

The application of the *waste of saw-works in manufacturing parquetry* must not be overlooked. Parquetry sheets are made in sizes of 59 cm. and 64 cm. square (24 and 26 ins.

square). The foundations for inlaid parquetry are made by gluing together strips of wood somewhat shorter than the dimensions of the sheet, cutting these glued pieces into the right length, grooving at the ends, and finally grooving and tonguing. In Russia another method is adopted; the foundations are made from a frame with two middle pieces and four panels. The frames are so morticed and tenoned that each piece has a mortice at one end and a tenon at the other. The four panels are grooved and tongued into the frames and the cross pieces, only the tenons of the whole work being glued. The panels are inserted so that the grain of the wood may run in one at right angles to the direction in the other. By this arrangement warping is made impossible and shrinkage is reduced to a minimum, since only the two parallel frame pieces in a total width of at most 25 cm. (10 ins.), under the most unfavourable conditions of temperature, can swell or dry to a small extent. All wood-waste may be used in making these foundations, since the panels have at most a length of 20 cm. (8 ins.). These parquetry foundations can easily be made by means of a few circular saws and a very simple boring machine for making the holes.

Sawdust for the Production of Stoppers. F. Koeller, of Neulengbach, in Lower Austria, has obtained a patent for a method of making stoppers from sawdust. The sawdust is rolled upon a round wooden rod, being made to adhere to the surface of the rod by means of some binding medium such as rosin or india-rubber cement. The rod has the same length as the layer of sawdust; the stopper furnishes a safe hold of the corkscrew in removing it from the neck of the bottle. Finally the stoppers are dipped to half their depth in pure melted paraffin, and are then ready for use.

Finally the *manufacture of fuel briquettes from sawdust* is to be mentioned. Molasses is recommended as an excellent binding medium for the production of briquettes from sawdust. The latter is moistened with the dilute molasses, the whole intimately mixed, then brought into cylindrical, rectangular, or other shape by means of suitable presses, and

dried. Colophony and tar may also be mentioned as binding agents. The prospects for the success of the manufacture of briquettes naturally depend, in the first place, on local conditions, especially on the regular supply of the waste material.

Both waste sawdust and wood are used in the manufacture of firelighters. The sawdust is mixed with melted rosin, or what is cheaper—common naphthaline—and pressed in moulds. Waste wood is cut into small strips which are tied or wired together in various ways, and also dipped in melted naphthaline to render them more easily combustible.

See also "Wood Products: Distillates and Extracts," by Dumesny and Noyer; and "The Utilization of Wood Waste," by E. Hubbard. (Scott, Greenwood & Son.)

CHAPTER XII.

CORK WASTE.

Utilization of the Waste of Cork-cutting.—The waste is either at once used for stuffing mattresses, for upholstery, or ships' fenders; or it is sorted, the adhering bark removed and applied to the same purposes; or it is converted into powders of varying degrees of fineness. The waste is first, by hand labour and sharp knives, freed from the outer rough and dark layer of the bark, then cut into sheets of different thicknesses, and finally into cubes of different dimensions.

The waste is also treated by filing or rasping, by which means a more or less fine dust is produced. It is easily comprehensible that increasing fineness of the cork dust considerably increases its price.

The woody portions of the waste, as well as the peculiar hard, sandy powder found in the cork, are partly separated by picking, partly by sieving, so that the remainder is, as far as possible, free from these impurities. Special machines are used for grinding cork waste, among which is to be mentioned the patented "Favorita" mill of H. R. Gläser, of Berlin. This machine consists of a cast-iron base, upon which is the real mill, with the grinding arrangements, the feeding arrangement, the transmitting disc, and the regulator. The mill works by reason of two conical surfaces, one solid, the other hollow, each provided with teeth of triangular section concentrically arranged, and engaging together. (One of the cones rotates, whilst the other is stationary and fastened to the framework. The grinding teeth pass by one another in such a manner that the material, introduced at the apex of the cone and driven by centrifugal force towards the base, is cut as if by shears, and crushed. The grinding surfaces

may be moved nearer together or farther apart by a hand wheel while the mill is working, so that the cork may be ground to different degrees of fineness. The teeth are fixed in segment-like plates, which are so arranged as to be capable of renewal; and according as the teeth on these segments are smaller or larger, near together or wide apart, the mill delivers finer or coarser cork. The velocity of the rotating cone also affects the fineness of the product.

Utilization of Cork Waste for Gas-making. Illuminating gas may be made in the usual manner, in closed retorts, from cork waste, 100 kilos (2 cwt.) of which give 50 cub. metres (1850 cub. ft.) of gas. The distillation is naturally much more rapid than that of coal. The illuminating power of the gas, with a consumption of 150 litres (5½ cub. ft.) per hour in the bat's wing burner No. 10, is thirty six candles, so that there would be a saving of 50 per cent, in comparison with coal-gas at the same price, in view of the greater illuminating power. The cork tar produced as a by-product is of the consistency of ordinary tar, and reddish brown in colour: on fractional distillation it gives 27 per cent of light oil passing over at 210° C., which consists mainly of benzol and toluol with a little naphthalene. The heavy oil contains anthracene and a little phenol. The liquid condensed in the gas manufacture contains methyl alcohol, acetic acid, and ammonia.

Cork Waste for Cork Mattresses.— In making these mattresses a fabric as waterproof as possible is sewed or glued together so that it forms a large sack, which is then filled with cork waste or coarse ground cork, sewn up, and then given the shape of a mattress by quilting. In order to make it quite impenetrable by water, the seams, and especially the quilted portions, are coated with an india-rubber solution, after the drying of which the mattress may be used. Mattresses for gymnasia are made in the same manner, but using an ordinary coarse fabric. Ships' fenders are bags or baskets filled with cork waste.

Use of Cork Waste in the Vinegar Manufacture. It has been recommended to replace wood shavings in the manu-

facture of vinegar by the much lighter cork waste. The elasticity of cork is made still greater by wetting, so that a sinking together of the filling material is not to be feared even in tall vinegar vessels. In the pores of cork are countless small organisms, and among them the acetifying bacteria exist in great quantity, so that the vinegar-making vessels filled with cork rapidly cause the formation of acid.

One of the chief uses of cork raspings is in the manufacture of linoleum and cork lino, for which purpose it is mixed with oxidized linseed oil and gum kauri in special kneading machines and is then spread upon cloth.

It is employed on a considerable scale for packing grapes in Spain and other countries where it is abundant.

Cork raspings also form an excellent non-conducting material, and for this reason are especially prized for filling the lining of refrigerator chambers and also as a non-conducting coating for pipes.

During the last few years cork raspings have also been made up into corks for bottles and for other purposes by mixing with a small quantity of a shellac solution in methylated spirit or in ammonia, or with a pyroxylin varnish, and pressing in moulds. These corks are excellent for many purposes owing to their regularity in size and outline.

CHAPTER XIII.

WASTE PAPER AND BOOKBINDERS' WASTE.

Utilization of Waste Paper. The waste paper¹ is thrown into a conical drum, about 10 ft. long and 3 ft. in medium diameter, covered by wire netting of three-quarter inch mesh; in passing through this drum the greater portion of the adherent dust is removed. Bones, pieces of wood, and other large hard objects, which announce their presence by striking the drum, can be removed by the workman who takes away the waste paper which has gone through the drum. On account of the dust, this sieve works in a casing lined with boards; it may be fed through the open narrower end or through a hopper; thirteen to twenty revolutions per minute are sufficient. The paper is next ground under edgerunners, and is then passed through a second sieving drum, somewhat smaller and covered with a No. 5 or 6 sieve. This drum is closed at the wider end (the exit) by a wooden bottom, which has two openings closed by slides. By this means the ground paper waste may be kept in the drum until all the particles of paper have passed through the sieve.

The residue, containing rags, thread, etc., which may be sorted and worked up, comes out when the slides are opened. This sieve, like the first, works in a wooden casing, one side of which is open, so that the sieved paper particles may be removed. It is driven at the side by bevel cog-wheels, so that it may be easily emptied; the speed is forty to fifty revolutions per minute. There is no loss of fibres in this method of purification.

Utilization of Bookbinders' Refuse.—The waste produced

¹ "Papierzeitung," 1886; "Neueste Erfindungen und Erfahrungen," 1886.

in bookbinding may well be used to prepare papier-maché for bas-reliefs, dishes, urns, picture frames, clock cases, etc. For this purpose all kinds of paper cuttings and waste cardboard may be employed. A second constituent is well-sieved wood ashes, especially those of hard wood; finally a third constituent is flour paste. The papier-maché is prepared from these substances in the following manner: The paper clippings and other bookbinders' waste are torn up small, thrown into a vessel filled with water, and left to disintegrate. Frequent stirring accelerates the dissolution. The disintegrated mass of paper is finally removed from the vessel, the water is lightly squeezed out, and the mass then comes into a mortar, where it is well pounded. Next it is taken out, laid on a strong linen cloth, and the water squeezed out as completely as possible. The balls of material obtained are then dried in the sun, near a fire, or in a stove. When dry, the balls are rubbed on a grater, when the particles of paper become similar in feel to cotton. They are then mixed on a board by means of a wooden spatula with ordinary flour paste and spread out with the rolling-pin, just as dough is worked.

This mixture with flour paste, which must amount to one-third of the whole quantity of material to be made, is formed into a ring on a board or table. Two parts of fine sieved wood ashes (best from hard wood) are placed in the middle, water is gradually added and mixed in until the ashes are thoroughly moistened. Finally the paper pulp is worked up with the wet ashes.

The mixture of the three constituents is now brought into the mortar and well pounded; it then forms papier-maché, and can at once be used. If the mass is to be kept moist for a length of time, it is filled into glazed earthenware vessels, which are placed in pairs, one upon the other, and protected from sun and heat.

From this papier-maché bas-reliefs can easily be made, the mass being used in place of the wax which otherwise is employed in embossing. For this purpose a portion is

taken out of the earthenware vessel, in which it is preserved, spread out flat to the requisite dimensions for the bas-relief, one side of the sheet so obtained is covered with flour paste and the mass then pressed upon a smooth surface—slate, polished wood, metal, or smooth pasteboard. Then a linen cloth folded in two is laid on the mass and superfluous moisture removed by repeated applications of the cloth.

After this treatment the design of the low or high relief can very easily be engraved on the mass by the embossing style; hollows can be dug out, and projections formed by adding fresh material where required.

This mixture has certain advantages over embossing wax. In the first place the style works much more easily in the soft paste, since the mass may be depressed, moved to all sides, raised, and moulded as desired. Should some spot begin to dry somewhat too soon, it is brushed over with a brush dipped in water, when the mass may be worked as before.

If the work is quite dry before it is finished, it may be moistened over a portion, or the whole, of the surface and further worked with the style.

After the finished relief is quite dry it is pasted over with thin flour paste by means of a camel's-hair brush, and then again allowed to dry, when the whole object is polished with a bone polishing-style. The object is now in a condition in which impressions of it in wax may be taken. It is then coated with thin size, again dried and polished as before. This last treatment of the surface permits of the application of oils or water paints, and of gold leaf simply by breathing on the surface or by using oil varnish. After painting or gilding the object it is usual to give it several coats of spirit varnish. After the latter is dry, neither heat nor cold, moisture, dust, or fly-spots can harm the work, for the varnished surface entirely protects the material beneath from injury. Dust is removed with a soft brush and fly-spots by a damp cloth.

Utilization of used Paper Cases.—By paper cases in this

instance are understood the small conical hollow cylinders of hard paper, similar in shape to cigar holders, which are used in the textile industries as yarn spools by weavers and stocking-knitters, and which are made in hundreds of sizes for various purposes and in different forms.

E. Höfel, of Gruna in Saxony, has patented a process for utilizing the large quantities of these paper cases in preparing articles of utility and ornament—umbrella and walking-sticks, fire-screens, baskets, card-tables, toy-furniture, picture frames, etc. The cylindrical, or rather conical, form of the cases makes their utilization easy. Just as the spindles on the spinning-frame must be exactly alike, so also the paper cases originally intended and solely used for the spindles are also exactly similar. One fits over another; the pointed cases may be pushed easily one into the other, and so form a rod already firm and of any required length.

After a number of the cases have been pushed one into the other, and a rod of the desired length obtained, a wooden stick or a wire of sufficient strength is drawn through the tube, in order to give it more solidity and afford a means of attaching the ferrule and handle. The ferrule and handle are screwed on the core at the bottom and top, and confine the bottom and top cases. The stick may then be painted and varnished. A pen-case is simply made from a large paper case, which is altered to fit its purpose by fitting a stamped metal bottom and a similar lid, and then ornamented by paint and varnish. In making containing vessels out of the cases, the so-called "ring-ousel" cases are laid near together and united at top and bottom by a ring of wire. They can then be ornamented in any required colour and a decorated top and bottom, preferably of sheet iron, applied.

CHAPTER XIV.

THE BY-PRODUCTS OF PAPER AND PAPER-PULP WORKS.

Utilization of Waste Matters in Paper and Paper-pulp Works.—The waste waters, produced in boiling, washing, bleaching, in the paper-machine and also in certain subsidiary operations, constitute the greater part of the by-products and require the most attention.¹ Fibres of all kinds, fine suspended mineral and vegetable substances, organic matter and colours in solution, and the chemicals employed constitute the impurities which are carried away in the waters. The most valuable of these substances are the fibres which originate in the various raw materials. In order to retain them, pulp-catchers of the most varied construction, settling-tanks, and also filters are used. The most convenient and the cheapest process consists in first allowing the waste waters to pass an efficient pulp-catcher and then to deposit in settling-tanks of sufficient size, of which several must always be provided, for alternate use and cleaning. These should be so arranged that the water can rise to a considerable height, and flow away smoothly over a considerable breadth, so that everything may be deposited in the almost motionless water. The separate compartments should be emptied at fairly frequent intervals, since, in consequence of the presence of the various organic matters in the deposit, decomposition readily sets in, which may extend to the fibres, with consequent loss of strength, or even destruction. The regained material is especially suitable for grey or dark packing paper. Since it consists of the finest fibres, it requires no preparation, but can at once be introduced into the paper-machine. If suitable papers are not made, this recovered fibre can readily

¹ J. B. Höhn, "Anzeiger für Papierindustrie," 1894.

be sold at a good price to pasteboard-makers. In this case it is rendered more suitable for transport by being pressed. The waste waters of cellulose works in particular carry away much good pulp, so that some arrangement of the kind described is very essential. As regards the separate divisions of the manufacture from which the waste waters are derived, the liquors of the rag-boiler are first to be considered; they contain so little fibre that they may be excluded from the fibre recovery. On the other hand, they are very rich in nitrogen, which results from the fat, perspiration, and other matters extracted from the rags, and since they also contain lime they produce an excellent fertilizer. For this purpose they are run into a pit, from which they can be withdrawn as required. The offensive odour is removed by gypsum, which also results from by-products. These waters may also be used for moistening the heaps of fertilizers which are composed of other waste products.

The waste liquors of cellulose works may differ in composition according to whether soda or sulphite-cellulose is made. In the former case the usual method for regaining the soda is employed, the very dilute liquors, which cannot profitably be calcined, being used to dissolve fresh portions of soda. For sulphite liquors there is not yet known a really useful and practicable process of recovery or of further treatment, in order to obtain tannic acid, sugar, or other substances. They can, however, be used for manurial purposes, after the free acid has been neutralized by alkaline or lime waste, which is always simultaneously produced. This is an inexpensive process, if conducted as mentioned above for the liquors from the rag-boiler. Where it has been tried, it has been found that all the liquors could be disposed of in this manner, and thus the nuisance of the waste waters entirely removed. Also this liquor, in consequence of the bisulphite and tannic acid it contains, is an excellent substitute for alum and sulphate of alumina in rosin sizing. It may also be used for the manufacture of brown and black colours.

The waters from the beating-engine are those from which

it is most important to recover the fibre. Those from the paper-machine, however, which contain clay, size, colouring-matters, and the like, which it may be necessary to conserve as far as possible, are best used over again several times by taking them back repeatedly to fill the beating-engine, to dissolve starch and clay, or to the rag-boiler. Since a certain quantity of water can only take up a definite quantity of foreign matter under given conditions, it is easily seen that the loss is considerably reduced in this manner. The composition of the paper is naturally very important. With paper which is not sized, coloured, or weighted, such a mode of treatment is unnecessary. In the case of the water from highly coloured paper, which would strongly contaminate the river into which it might flow, it would be advisable to beat and wash the rags from the boiler with it, by which means the colouring matter would be partially fixed and partially destroyed. The bleaching-powder residue is also to be considered along with the waste waters. It cannot be employed as manure. It is best collected in a pit and converted by stirring with soda solution into calcium carbonate, or with sulphuric acid into gypsum, either of which may be employed as a fertilizer, especially when mixed with the above-mentioned liquors, or they may be used as fillers if the residue is pure. Carbonate of lime, which is less suitable for use as a filler, may be converted into quicklime in a small lime-kiln.

According to Siedel, the waste liquors from the sulphite-pulp works, in which the Rittner-Kellner process is employed, have a sp. gr. of 1.050 and contain 11.44 per cent of solids; the total sulphur is 9.54 per cent, 93 per cent being present in organic combination. The amount of potash in these liquids is about 1 part in 5000. The liquids are evaporated and incinerated for the recovery of the soda, of which, according to F. Briggs, 85-90 per cent is obtained.

According to K. Lorentz,¹ the waste resin obtained by treating the waste lyes of paper-pulp works with acids, a

¹ "Seifensieder Zeit.," 1916, 43, 501-502.

product which at one time was quite unsaleable, now finds a market at about 4½d. per lb. It can be purified by treatment with acid or with lime, and can be saponified or distilled. It is of no value for soapmaking, but can be used for paper-sizing and possibly in varnish manufacture.

Of less importance are the residues of rosin, colour, and china clay, but if they have accumulated or are produced in large quantity, they are mixed, allowed to dry in the air, ground with a suitable filler on an edge-runner mill, and used as a substitute for earth pigments for common papers. An excellent earth pigment, as a substitute for dark ochres and umber, may be obtained in sulphite-cellulose works by treating the burnt or spent pyrites, which consists to a great extent of ferric oxide. The material is first broken up under stamps to the size of hazel-nuts, the finer portion being then sieved off and levigated. There results a very fine, soft colour of great staining power. In view of the quality of the material, the levigating apparatus may be of very primitive construction, the cost of working consisting only of the labour, the process being quite remunerative. The larger pieces which remain are composed mostly of unburnt pyrites; these are taken back to the furnace.

The grey arsenic sublimate is to be regarded as an unimportant by-product of cellulose works; it is deposited in the gas flues and is generally disposed of in the wash waters. This is extremely destructive to fish, even at very great dilutions—far more so than any other substance in the waste liquors. The deposit is formed in the pipes in solid form, so that it can readily be collected; in large parcels it always finds purchasers. As a result of the frequent blowpipe solderings there is gradually formed in the gas-producing apparatus a residue of cadmium, an uncommon and dear metal which, in other branches of industry, is collected for utilization. Finally, calcium monosulphite and gypsum separate from the sulphite liquor on standing, and also on boiling. The former can be used as a solid "antichlor," when it is converted into gypsum, or it may be mixed with the fertilizers

already mentioned; also it may be converted by sulphuric acid or a warm solution of sodium sulphate into gypsum, or by soda into calcium carbonate, in which last case it is again used in preparing fresh boiling liquor; it is also used for this purpose without treatment, but since it is not finely divided, but is generally caked together and encrusted, it has not been found very suitable.

The residues of the soda recovery, i.e. of causticizing, in the soda-cellulose works are of particular importance—in the first place, because of their great quantity. This by-product consists essentially of carbonate of lime, contaminated by soda, carbon, and other matters. It is best utilized by burning after it has dried to a certain extent, the requisite quicklime being thus reproduced. In consequence of the large quantity to be dealt with, continuous working is necessary, and thus fresh lime is continually produced. For conversion into gypsum the by-product is treated with sulphuric acid; the soda salt must be completely neutralized if the gypsum is to be used as a fertilizer.

Certain by-products, which do not come in contact with water, are produced in wood-pulp and cellulose factories, viz. the waste—sawdust, bark, and other pieces of wood—obtained in cutting and dressing the wood. The sawdust constitutes an excellent fuel when burnt in specially constructed grates; the bark is used as litter for cattle, and is in demand for this purpose by farmers. The two substances together can be worked into a species of cellulose, an operation which is only found profitable when collected in boilers specially constructed for the purpose. Chance pieces of bark, larger pieces of wood, the waste from the grinding apparatus, and the dust from the sieves cannot profitably be separately treated.

As previously stated, however, waste wood is best distilled for the production of wood spirit, acetic acid, wood tar, and charcoal.

The last waste product to be mentioned, but the first in the actual manufacture, is the rag dust, which by itself con-

stitutes an excellent fertilizer. The fibre it contains may be extracted by agitating with water and running off the liquid after a short time, when the fibre is carried away, but the dust, sand, and heavier particles remain behind.

The damaged paper is also to be reckoned as a by-product. It is unnecessary to say much concerning its utilization, except that it is taken back to the beating engine: it is always produced in every process; it is only mentioned as an example to demonstrate that the further treatment of waste matters is usually profitable, and occasionally distinctly so. Utilization of all waste products is an important factor in the balance sheet of a paper or paper-pulp works, and increases in importance as time goes on.

Paper from Corn Stalks, etc.—It is estimated by C. J. Brand that the following wastes are available for paper-making:—

	Tons.
Corn stalks	30,000,000
Ricestraw	1,500,000

but in addition there is flax straw, megasse, or bagasse (sugar-cane refuse), cotton-seed hulls, etc., to a very large amount.¹

Recovery of Wax.—After preparing the fibre from raffia, esparto, and sugar cane, the residues are extracted with solvents and waxes obtained thereby.

See also "The Paper Mill Chemist," by H. P. Stevens; and "The Treatment of Paper for Special Purposes," by L. E. Andés (Scott, Greenwood & Son).

¹C. P. Cross, "Lectures on Cellulose," Institute of Chemistry, 1912.

CHAPTER XV.

THE WASTE PRODUCED IN THE MANUFACTURE OF PARCHMENT PAPER.

Utilization of Parchment Paper Waste.—C. D. Cech has given an account of the utilization of the waste from parchment paper-works in the preparation of oxalic acid. He remarks that the chief attention in making oxalic acid from parchment paper waste must be devoted to a thorough washing of the latter. According to the method of manufacturing oxalic acid introduced by Roberts, Dale & Co., of Warrington, by fusing sawdust with caustic potash (see p. 80), parchment paper waste will not only give a sufficient yield of oxalic acid, but its preparation from this material would not suffer any drawback such as occurs with the colouring matters which arise in the treatment of hard woods.

The process of manufacture is the same as in the preparation of oxalic acid from sawdust (compare the details of this application of sawdust).¹ J. Upmann remarks, with regard to Cech's proposal, that the process of converting cellulose into oxalic acid by fusion with alkali is no novelty, since it had already been confirmed by experiments on the small scale, before the introduction of the present method of making oxalic acid from sawdust; on the other hand, it must be admitted there had been no previous published proposal to utilize cellulose in this manner. Now, Upmann considers that the question whether parchment paper waste may really be a suitable substance to replace sawdust cannot be decided *a priori*, since, even if sufficient raw material could be obtained, which is doubtful, it would have to be compressed for transport to a distance: whilst the complete washing would

¹ Post's "Zeits. f. d. chem. Grossgew.," II, 4.

be attended with more difficulty than would appear at first sight. Also, the subsequent drying of the paper could not very well be obviated; thus an expense would be incurred which is lacking in the case of sawdust; this might, however, be compensated for by a larger yield of oxalic acid.

CHAPTER XVI.

WOOL WASTE.

*Utilization of Waste Wool in making Shoddy, etc.*¹—

For this purpose rags and other waste containing woollen fibre, as well as mixed fabrics of cotton and wool, are employed. The rags and waste are first subjected to certain preliminary operations in order to remove buttons, seams, string, etc., when about 20 per cent of waste is produced, which is used in agriculture. The rags are then cut into pieces of suitable size, and sorted, first into pure woollen and mixed fabrics, and subsequently according to the character of the wool fibres, whether those are short or long. The short-fibred rags consist mainly of cloth and similar materials of carded yarn, milled or otherwise; the long-fibred consist of the unmilled, and especially of worsted, fabrics. The names mungo and shoddy are used respectively for the materials thus differentiated, after they have been torn up. Finally, the rags are sorted according to colour.

In the following description we proceed exactly according to the authorities quoted. Since rags come into commerce unsorted, or only superficially sorted, it falls to the manufacturer to undertake the operation. This operation is, however, a very necessary one as it loosens the dust in the rags, the air of the sorting-room soon becoming more than saturated with it; good ventilation is accordingly requisite, unless the rags are first cleaned. Breton, of Pont de Claix, accomplishes this purpose by arranging the rags in a layer 30 cm. (1 ft.) deep and moistening them with bleaching-powder solution, 0.5 litre per sq. metre (1 gal. per 100 sq. ft.). They are then brought into a species of corn-sifter provided with a fan,

¹ Grothe, "Technologie der Gespinnstfasern," vol. i., p. 209 *et seq.*; Muspratt, "Prakt. Chemie," vol. vi.

which drives out the dust into a flue 5-6 metres (16-20 ft.) long, where it deposits. Leading into the outlet is a water-pipe, which yields a fine spray of water which throws down

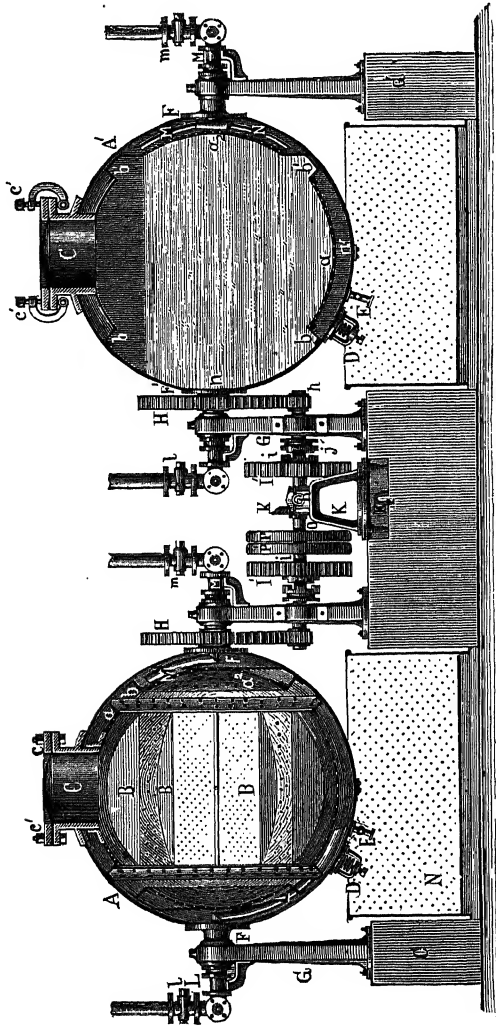


FIG. 9.

all the dust. Dirty rags are boiled with milk of lime and a little soda, washed in a washing-machine, and then dried. A rag-washer, which works very well, has been constructed

by Planche & Rieter.¹ This machine, which is made by Seraphin, of Paris, consists of two spherical vessels for the reception of the rags; these may be worked together or separately, for which purpose the driving mechanism is provided with the requisite clutches.

Fig. 9 is a vertical section through the axes of both vessels, Fig. 10 a ground plan, and Fig. 11 an elevation, of the driving mechanism. In Fig. 9 is shown the different systems used for introducing the steam and the cleansing liquid, the various possible modifications being represented at the same time.

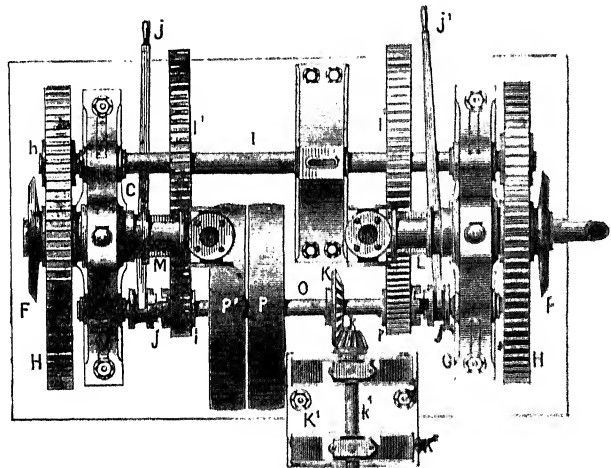


FIG. 10.

Each of the spherical vessels *A* and *A'* is about 6 ft. in diameter, holding about 1300 lb. of rags, and is constructed of 2-inch boiler-plate, so that it is capable of resisting a steam pressure of five atmospheres. Each also contains a double perforated bottom of thinner plate *a*, fastened to the outer walls by angle irons *b*. The holes in these double bottoms are $\frac{5}{16}$ in. wide, placed at distances of 1 in. apart. Over this bottom are scrapers *B* or rods 18 ins. long, which separate the rags and keep them in motion. The steam enters the ring-shaped space *a'* between the perforated bottom and the outer

¹ "Polyt. Centralbl."

wall. The manhole *C* attached to the vessel serves for the admission of the rags and for necessary repairs; it is closed by a cover fastened down either by ordinary bolts as shown on the vessel on the left, or, as seen on the vessel at the right and in Fig. 12, by a swinging nut *c'* moving on a hinge. The valve *D*, shown magnified and in section in Fig. 13, is also affixed to the exterior of each vessel; it serves as a safety-valve against too strong pressures, and may also be used to

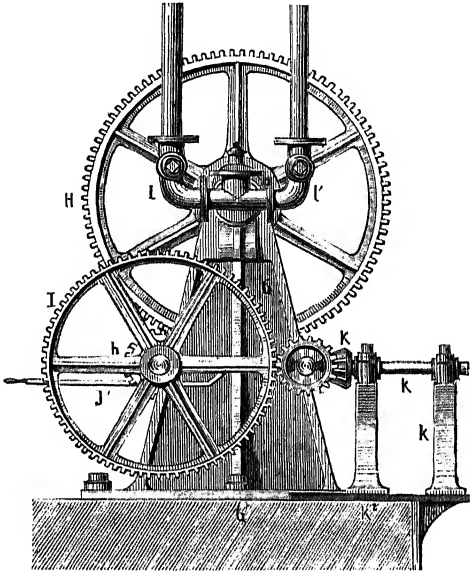


FIG. 11.

admit air in case a partial vacuum should be produced. It has a brass seating, fitting on to the spherical vessel, in which moves the real safety-valve *d*, provided with a conical face tapering downwards and pressed down by a strong spring *e*, which works against the plate *f* of the arch *D*, which again carries a screw *f'* for regulating the pressure of the spring. The valve *d* is again in its turn perforated and carries the second valve *d'*, opening inwards, which is kept pressed into its seat by the weak spring *e*.

A tap *E* on each vessel, opposite to the manhole, serves

to run off the liquor or washing liquid. Each vessel has two pinions F and F' , which are carried by the columns G bolted to the brick-work G' . The longer axis F' carries a large cog-wheel H , which is actuated by the cog-wheel h . Both the wheels h are on the shaft J , which has its bearings in the columns G and in a third and lower one. The main shaft O , with the pulleys P and P' , moves the shafts I , etc., by means of the cog-wheels i and i' . In order that each vessel may be revolved separately, the cog-wheels i are not attached to the shaft O , but are made to rotate by means of the clutches j and j' , worked by the levers J and J' . Further, in order to be able to move the vessels by hand so that the manhole may be exactly at the highest or lowest point, in order that the rags can be introduced or removed, the conical

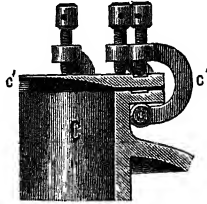


FIG. 12.

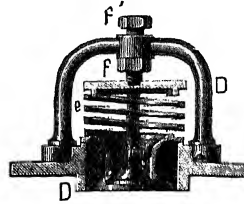


FIG. 13.

cog-wheel k is also attached to the shaft O . It is moved from the subsidiary shaft K' to which a handle can be attached, and which is supported on bearings in the supports k^2 . From Fig. 9 it will be seen that the steam and the various washing liquids can be conducted through the hollow axes F' and F'' in various ways. On the left side of Fig. 9 there is a central pipe L which rests in a small support and divides into two branches, provided with the taps l and l' (Figs. 9 and 11), in order to be able to cut off the supply to either. In the interior of the vessel is seen the pipe L , continued downwards by the pipe L' , which terminates between the outer wall and the perforated bottom and rotates with the vessel. The fixed pipe M enters through the other axle F'' ; it also divides outside into two branches with taps m and m' , whilst the other end is continued inside by the arm M , which

points upwards. A perforated diaphragm a' at the side protects the pipe from contact with the rags. The steam enters through this pipe at a pressure which can be regulated as required.

The pipes affixed to the vessel on the right are differently arranged. The steam there enters on the left through a rose n . On the opposite side are to be seen two fixed pipes M and N ; M being directed upwards introduces the steam, N downwards and introduces or removes the washing liquid. Both these pipes are connected by a T-piece with the central pipe M which passes through the axle B' , and is separated by a diaphragm into two divisions. The inside pipes M and N are here also protected from the rags by a perforated wall almost concentric with the spherical vessel and somewhat differently fixed. A tank N perforated by many small holes is placed under each vessel. It may be fixed on wheels so that it can readily be moved on a tramway. It is intended to receive and drain the washed rags when they are turned out of the boiler.

These machines work in an exactly similar manner to the ordinary cylindrical form. When in the position of Fig. 12 they can be filled through the manhole, which is then closed tightly. When the washing is finished, the liquid is first run off through the cock B ; the sphere is then turned so that the manhole is at the bottom. The latter is then opened, and the rags fall out.

It is necessary to produce a constant uniform steam pressure, which is effected by means of the regulator, shown separately in Fig. 14. It consists of a vessel A with a cylinder C cast on at the top, and with two side pipes B and B' placed opposite to one another, of which B' is used to carry away the steam, whilst a safety-valve S is attached to B . The cylinder C is provided with a bored metallic lining, in which works the double piston pp' . Between the two discs of the piston communication is made with the vessel A by means of the side passage a , the opening of which is opposite to the pipe c . The top of the piston is connected by the rod l with

the lever *L*, on the end of which is an arc *s* to carry the weight *P*. When, for example, the safety-valve is loaded to four atmospheres pressure, and this is not to be exceeded, the weight of the lever *L* must be so regulated that the space between the two dics of the piston provides a full communication between the channel *a* and the entry pipe *c*. If, say, steam of six atmospheres enters, the piston rises, and the openings of *c* and *a* are shut off to some extent so that little steam can enter the vessel *A*. The safety-valve *S* serves to prevent any accidental accumulation of pressure.

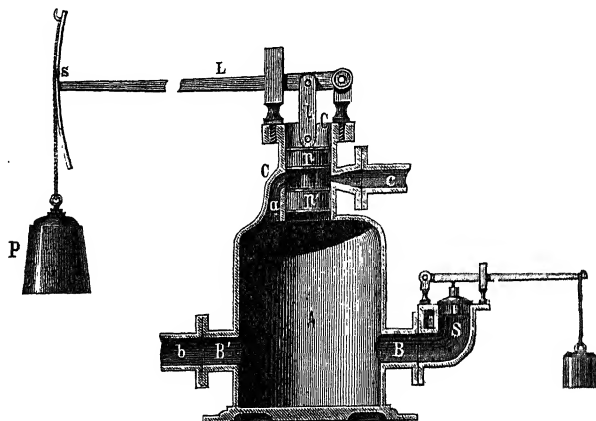


FIG. 14.

Grothe states that according to the mode of operation there are four different methods of manufacturing mungo and shoddy:—

1. The woollen rags, unwashed but slightly moistened, are torn up, and without further treatment in the carding-machine are at once put on the market. The loosened mass thus still contains all the dust and dirt.

2. The woollen rags, without being washed before tearing, are afterwards treated dry in the carding-machine, by which treatment a quantity of dust is removed.

3. The woollen rags, without washing before tearing, are afterwards slightly oiled and carded. This system affords

the greatest opportunities for fraud. In the first place, the oil fastens the dust on the fibres, besides which it serves to retain the fibres which are too short for further treatment, these being like dust as compared with the longer fibres. When this carded mungo comes into the market it generally deceives the purchaser. It is different when the mungo manufacturer spins it himself.

4. The woollen rags are well washed before tearing, and afterwards are not oiled or carded. This method always produces a very clean and unmixed fibre, free from all impurities. It also avoids the production of dust, which injuriously affects the workpeople in the other methods.

The process of treatment has now been outlined. After freeing from buttons and seams, the rags are put through a rag-shaker which removes dust and dirt; they are then sorted into different qualities, cut into small pieces, and fed into the "devil," which tears them into fibres. This procedure is adopted in methods 1, 2, and 3; but in method 4 the rags are washed before tearing, and again afterwards, then centrifuged and dried. The "devil," or tearing-machine, consists of a large drum, the exterior surface of which is thickly studded with iron teeth, and which moves with considerable velocity - about 550-700 revolutions per minute. The rags are fed to the drum between two rollers of small diameter provided with longitudinal grooves. These rollers revolve very slowly and, since the upper is pressed very hard on the lower by means of a lever and weight, the rags are held fast and the teeth of the drum comb out only the cross threads. This operation produces a fibrous mass, which is termed mungo when it originates in cloth or carded yarn fabrics, and shoddy when it is produced from worsted and long-fibred materials.

In the above methods a treatment in the willy carding engine follows after the tearing by the "devil". The rollers of the former have strong wire points with an elastic attachment to the surface. Mungo is generally not subsequently treated in the willy and the following carding-machine, but is at once packed and afterwards carded mixed with natural

wool in proper proportions, since it is too short in the fibre to be spun alone. The proportion of mungo varies from 20-70 per cent to 30-80 per cent of natural wool. The subsequent spinning offers no further difficulties. Shoddy wool is at once carded on the willy and the following machines, and is generally spun without further additions.

There is a great quantity of rags composed of mixed fibres. Generally the warp is of vegetable fibre and the weft of animal fibre. For mungo-spinning, the vegetable fibre must be removed. Usually the two textile fibres are separated by treating the rags with acids, which destroy the vegetable fibres, but do not attack the wool. For this purpose sulphuric acid diluted to about 18° B. is used, and also hydrochloric acid. After the acid bath the material is brought into alkaline solutions, in order to neutralize the acid remaining in the fibre; it is then well dried. In consequence of this treatment, the vegetable fibre becomes converted into a friable condition, whilst the wool fibres remain uninjured, and can be isolated simply by rubbing. For this operation, many different methods are now employed, which will be mentioned below.

Newmann separates the wool from mixed woollen fabrics as follows: In order to protect the wool from the action of the acid, it is saturated with a solution of sulphate of alumina or alum (1.5 parts to 100 parts of water), and then dipped in a warm soap solution containing 1.5-7.5 parts in 100 parts of water. The material to be treated, after this preparation, is brought into sulphuric acid (1.5 parts diluted with water to 100 parts). The moist fabric is then subjected to a temperature of 95° C. The vegetable fibre is thus thoroughly disintegrated and can be removed by rubbing or washing in hot water, the wool fibre, however, remaining unimpaired.

R. Böttger omits the preliminary treatment with alum, but applies a soda bath after the treatment of the fabric, in order to neutralize the acid. The carbonic acid, thereby evolved, considerably loosens the residual wool.

Ward gives a process for separating cotton from wool,

which has for its object the recovery of the cotton for paper-making. He subjects the mixed fabric to the action of water under a pressure of from three to four atmospheres in a Papin's digester. The cotton then remains quite unaltered, whilst the wool is converted into a friable substance.

In order to recover the woollen fibre from a fabric* composed of wool and vegetable fibre, Schaller immerses it for 12 hours in a bath composed of 3 per cent of sulphuric acid (66° B.) and 97 per cent of water, and then dries. If this solution should not act sufficiently energetically, the rags are exposed for from 4-5 hours to a temperature of 60-70° C., when the vegetable fibre becomes friable.

Rowley recovers the wool from mixtures with vegetable fibres by treating the rags with dilute sulphuric acid, subsequently bringing them into a rotating wire sieve, in which they are dried by a current of hot air. The rags are then packed in boxes with sand, where they remain for a longer or shorter time, according to their nature; they are again separated from the sand by the rotatory action of the wire sieve. This method is so complicated, and its effective action appears so questionable, that it can in no way be recommended.

Grothe calls attention to the fact that the greatest care must be given to the strength of the acid bath, in order that the wool hairs may not be attacked.

Extracted mungo wool is mixed with mungo obtained by the mechanical methods, and the two worked up together.

The shoddy or mungo is mixed on a floor with varying quantities of fresh wool and with considerable quantities of oil, usually recovered oil, then put through the usual carding, spinning, and weaving operations for the manufacture of cloths to be sold at lower prices than would be possible when using all new wool.

Manufacture of Yellow Prussiate of Potash from Wool (horn and blood).—J. J. Hess, of Vienna, has given a very full account of his own experience of this manufacture.¹ "The proper preliminary treatment is exceedingly im-

¹ "Deutsche Gewerbe-Zeit."

portant to lucrative working, consisting in a cautious drying at a high temperature, or rather in gently calcining the nitrogenous material, in order, in the first place, to drive out all moisture and, in the second, to render the nitrogenous matter more easily pulverizable and also richer in nitrogen. This process of concentration is best conducted in a kind of "fig-coffee" drum, or in a large rotatory apparatus, capable of being heated. One axle of this machine must be hollow, and be connected, by means of a bent pipe, with a cooling tank, which condenses the vapours evolved, since these are also valuable, consisting as they do of combustible oils and ammonium carbonate.

The dried, roasted, and concentrated mass, when the operation has succeeded, must be frothy, brown, transparent, interspersed with bubbles, of a slight, peculiar odour, and very easily friable. If too strongly burnt, the mass appears black, is very light, very frothy, and very poor in nitrogen; on this account every attention must be given to the drying process, in order that heavy loss may not result.

The next important material is the potash, which is frequently, through false economy, bought at the lowest price, and, being of poor quality, adds a good deal of inconvenience to the manufacture. The potash should be as pure as possible.

Next comes the third raw material, the iron, which can be used in the form of hammer scale, dull-coloured ferric oxide, or iron filings and turnings, in fine powder.

All the substances should be dried and kept in that condition, and in a state of fine powder; they are then mixed for use in the following proportions: 10 kilos of dried horn, etc., 6-8 kilos of potash, 4 kilos of hammer scale, etc., the average yield from these quantities being 3-3½ kilos of yellow prussiate.

The intimate mixture is now heated in clay crucibles lined with sheet iron, in a muffle furnace very similar to an ultramarine furnace. After about 24 hours the furnace is opened, the crucible removed, and the coherent mass, which readily falls out, thrown at once into cold water in order to

prevent oxidation. As soon as the mass falls into the water a hissing is heard, and frequently sparks momentarily fly out, which is a sign of a successful operation. The mass soon falls to a fine, black powder, leaving a clear, pale yellow solution, which becomes dull in colour when subsequently boiled, and deposits fine crystals of ferrocyanide of potassium on standing.

In addition to other advantages, Hess's process also utilizes the resulting fine powder. The black deposit contains pure iron and carbon; the iron can be extracted by nitric acid and used in the preparation of Prussian blue, or it can be transformed into ferric oxide by burning in the air, and used over again. The nitrate of iron, which is thus obtained, may be acidified and used to act on the mother liquors, when Prussian blue and potassium nitrate are obtained. The carbon left in very fine powder, after the iron has been dissolved out, yields an excellent pigment; after washing and grinding it has a fine colour with great covering power.

Recovery of Oil from Wool. Preparation of Suint.—

There are two methods of extracting oil from wool, the one by means of solvents, the other by soap or alkalies and water. In the former process the wool is treated in large closed tanks, in the same way as bones, with volatile solvents such as benzine, benzol, and carbon bisulphide. In recent years carbon tetrachloride has come much into favour as a solvent owing to its non-inflammability, freedom from odour, and easy volatility, as well as other similar substances, trichloroethylene, dichloroethylene, etc. The solvent is evaporated from the fat in a still leaving a residue consisting of "suint" or wool fat mixed with dirt, etc., which latter is removed by pressing in bags at a moderate temperature.

The wool fat or "suint" thus obtained is further purified and is used as an ointment mass under the name of "adeps lanae," or mixed with about 25 per cent of water as "lanoline," very useful in preparations for the skin.

Suint and also the potash contained in the wool can also

be recovered by the Smith Leach process from wool-scouring waters by evaporation and centrifugalization.

Potash from Wool Sweat.—According to the patent of Prof. K. Kraut, of Hanover, wool is washed in the ordinary washing-machine with warm water, to which potash (pearl-ash) is added. The wash waters are allowed to settle in tanks, the residual liquid being evaporated to dryness, and heated on the hearth of a reverberatory furnace. The residue contains the potash used in washing, and the potassium which was present in the sweat, also mainly in the form of carbonate of potash. A portion of the potash solution obtained by lixiviating this residue is again used for washing wool, whilst the remainder may be evaporated, and the residue calcined, forming crude potash from which pearl-ash can be obtained.

The residual waste from shoddy which cannot be otherwise utilized is converted into manures. A sample of "Ground Wool" gave the following figures on analysis:—¹

Moisture	7.92
Organic matter	70.52
Alkaline salts	0.56
Phosphates	0.92
Oxide of iron }	3.96
Alumina }	
Carbonate of lime	5.54
Sand	10.54
	<u>100.00</u>
N = to Ammonia	7.56

¹ Ivison Macadam, "Jour. Soc. Chem. Indt.," 1888, p. 95.

CHAPTER XVII.

SILK WASTE.

The Utilization of Silk Waste.—The patented machine of Grothe and Heller remains the only one hitherto made for the manufacture of silk shoddy from silk rags, since it has been found that the quantity of silk rags is not great, and that the fabric cannot be entirely unravelled on account of the strength of the fibre. (Compare also the article on Shoddy, p. 106.)

Broadly speaking, there are three branches of silk-waste *spinning*, which involve the manufacture of “floret” silk from first waste, *noil yarn* or “bourette” silk, and *silk shoddy*.

The first raw material to be mentioned is the strusa, i.e. the clean waste obtained in unreeling the cocoons, which were unreeled from fire or steam-heated basins. Strusa à vapeur is accordingly the more valuable, and in greater demand, to which also the fact contributes that it is produced in larger quantities of uniform quality, since it is made in the larger works.

Perforated cocoons and whole cocoons which cannot be unreeled are not included in the strusa; these are brought into commerce under the term of “cocoons”.

Strazza is the name of the waste produced in spinning raw silk, through the breaking or spoiling of the threads. These materials also occur in a slightly decayed condition, the decay being said to improve the quality.

The second commercial raw material is decayed waste-stami, *peignées*, the stami being somewhat decayed cocoons. Marseilles is the principal market for silk waste, the following commercial qualities being sold there at prices rising from

1 franc to 16·5 francs per kilo (4½d. to 6s. per lb.): Bassinets, Moorish, frisons de nouca, de Rhorassan, Syrian, Accoulys (Greece), French, Italian, Persian, Broussa, Oshio, Yama en Flottes, Kibisso Yama, Bourre de Chine, Levant, Spanish, Adrianople, Salonica.

The damaged cocoons are placed in deep vats, hot water is added, and the mixture allowed to stand for several days. The dead pupæ quickly cause putrefaction, which attacks and destroys the gummy and resinous matters. The material is then smoothed and cleaned by a combing-machine, and brought into the market under the name of peignée, the fibres of which are from 5·16 cms. (2-6 ins.) in length.

The flocks and unspinnable waste obtained in spinning the first waste have been utilized by Pasquay for spinning into round hemp cords, and plaiting the cords, thus obtaining long bands, which can be used for wrapping steam-pipes to prevent loss of heat.

CHAPTER XVIII.

THE WASTE WATERS OF CLOTH FACTORIES.

Utilization of the Waste Waters in Cloth Factories. It is well known that the waste waters cause the fouling of the streams into which they run, and are, on that account, often a source of great inconvenience, and frequently a restraint on the manufacture. This is especially the case in flat countries, such as Holland, where—as, for example, at Tilburg—the endeavours to remove the stagnant waste waters, in this case on sanitary grounds, have been extraordinary. According to the method of E. Schwamborn, of Aix,¹ the waste waters of cloth factories are used to prepare lime soaps, the process being as follows:—

Attempts at clarification, by means of sand or cinder filters, in the so-called clarifying vats, have proved unsuccessful, on account of the mechanical difficulties in separating the soap, though they may have succeeded with the solid suspended impurities. The soap may be removed by chemical means, when not only is the water rendered clear, but the fatty matters contained in it may also be regained. Schwamborn's process is applied in a similar manner to the recovery of the wool-fat from the waste waters of wool-washing. The waters used in fulling and rinsing the cloth are included under the head of waste waters. They contain the oil used in spinning, to the extent of 15 per cent of the weight of the yarn; the soap used in fulling, up to 30 per cent of the weight of the cloth; also the size used for strengthening the warp, and, in addition, dissolved colouring matters and wool fibres. The clarification of these wash waters depends upon their decomposition by means of milk of lime, the following being a description of the method of treatment:—

¹ "Dingler's Journ.," 216, p. 517.

The washing-machines are provided with two waste-pipes—the one to conduct the first thick liquid, which is gradually becoming more dilute, into the collecting-tank; the other, for the direct removal of the next clear waters, which are fit to run direct into a stream. When the collecting-tank, the capacity of which is assumed at 150 cub. metres (5295 cub. ft.), is full, which takes about fourteen days with a consumption of 2000 lb. of soap, corresponding to the washing of about 8000 lb. of cloth, its contents are run off through a pipe at the bottom, into a tank of equal size at a lower level. At the same time a thin stream of milk of lime is run from a vessel (a vat provided with a tap) at a higher level, into the outflow pipe, so that an intimate mixture is obtained. Sloping ground is an advantage for this arrangement; but when no slope is available its place must be taken by pumps.

The bottom of the second tank—the decomposing tank—is made of three layers of bricks. The lowest is continuous; in the next, the bricks are laid with as great interspaces as the third layer, which is also continuous and united with mortar. This system of drains has an inclination towards one corner of the tank, where it communicates with a wooden funnel reaching to the top of the tank, and provided with a slanting series of holes, which are closed with wooden plugs whilst the suds are being admitted.

The decomposition takes place immediately the liquids enter the tank; the lime soap separating in flocculent form surrounds the solid suspended substances, such as colouring matters, wool fibres, etc., partly sinking with them gradually to the bottom, where it finally unites to form a precipitate. Even a few minutes after mixing the uppermost layer of the liquid is free from the precipitate, and not only clear, but also colourless. This clarification, which extends to the dissolved as well as the suspended colouring matters, is so energetic that considerable quantities of some dye waters may be added and simultaneously purified. The characteristic appearance of the flocks in the clear water affords a sign of a sufficient

proportion of lime : slight excess, however, does not hinder the purification. For 150 cub. metres (5295 cub. ft.) of the suds, there is required approximately 0·3 cub. metre (10·6 cub. ft.) of lime paste, in the condition in which it occurs in wet slaked lime, the quantity naturally varying according to the amount of soap in the suds.

The clear water is run off by drawing the wooden plugs, fixed in the funnel, from above down to the point to which the thick lime soap is found to have settled. The manipulation is easier if a board partition, also provided with plugs, be placed transversely in front of the funnel, up to half the height of the tank. More water is removed, partly by evaporation, which is assisted by the cracking and shrinking of the mud, and partly by filtration in the system of drains at the bottom. After several days, the substance lying at the bottom is a dried fissured paste, which is thrown out on the edge of the tank, and spread, in order that it may dry further. In winter, when necessary, the final drying takes place under cover on suitable supports. If the space at disposal permits a second decomposing tank to be laid down, the drying is made considerably easier, by reason of the double time allowed.

The lime soap retains the last portions of liquid for a long time, whilst, on account of its greasy nature, i.e. its want of incompatibility with water, it does not again take up water, such as rain, which may reach it. A lump, after drying in the air, may lie for days under water without appreciably gaining in weight. The residue from a tank 1·5 metre (4 ft. 11 ins.) deep, is about 6 cms. (2·4 ins.) thick, which corresponds to 4 per cent of the liquid.

From statistics it is calculated that the yearly quantity of cloth washed in Europe is about 10,000,000 cwt. Now, 8000 lb. correspond, as stated above, to 5295 cub. ft. of water, or to 2000 lb. of soap, and include 800 lb. of oil used in the spinning (calculated at 10 per cent of the weight of the cloth). There are obtained on the average about 1600 lb. of lime soap. Accordingly the soap waters of Europe corre-

spond to about 2,000,000 cwt. of lime soap per annum, which is produced from 2,500,000 cwt. of soap, containing 45 per cent, or 1,125,000 cwt. of fatty acids, and from the oil used in spinning, 10 per cent of the weight of the wool, or 1,000,000 cwt. of fatty acids. Thus, there is a total of 2,125,000 cwt. of fats annually used in European cloth factories.

The lime soap is insoluble in water; it dries to a pale dark-grey substance, which can easily be cut, has a fatty feel, and burns with a flame when lighted. By decomposing the lime soap with acid, and then washing with hot water, a fatty substance is obtained, which may be directly subjected to distillation, the distillate separating on pressing into solid and liquid fatty acids.

For the *treatment of the suds of wool-washing and cloth fulling*, E. Neumann, of Rosswein, has obtained a patent.¹ In this case the whole apparatus consists of two tanks dug in the ground (even for large factories two oil-vats of 12-15 cwt. capacity are sufficient), into which the suds are run by sluices or pipes from the washing-machines or cylinders, and also of a lift and force-pump, and a filter-press with waste channel.

Crude calcium chloride (or some substitute, which forms, with fats, soaps insoluble in water) is dissolved in an equal weight of water and the solution, to the extent of 1, 1.5, or 2 per cent of the total capacity, according to the amount of fat in the suds, poured into tank No. 1. The suds are then run in, the ensuing commotion ensuring a thorough admixture with the calcium chloride solution; the lime soaps are at once formed and separate in flocks, which remain suspended in the water. When the first tank is full, the contents are pumped into the filter-press, whilst in the meanwhile the suds are being run into the second tank, which has just previously been charged with the necessary amount of calcium chloride.

In the filter-press there remain lime soaps, dirt, hair, etc., whilst the clear water, carrying with it chiefly potassium and

¹ "Neueste Erfindungen und Erfahrungen."

sodium salts and a little excess of calcium chloride in solution, runs away by the waste pipe. After tank No. 1 is emptied, tank No. 2 is pumped out, No. 1 again filled, and so on, until after about eight to twelve hours' work the press is full, a condition readily recognized when the taps almost cease to drip. The press is opened, and the cakes, when they do not fall out unassisted, removed by a wooden spatula. The press is then closed, and the pump again started, when the process again commences. Only the introduction of the calcium chloride, the opening and closing of the feed-cocks, the removal of the press-cakes, and the starting of the pump, require manual attention; these operations are the work of but a few minutes, consequently a special workman is not requisite.

The press-cakes obtained are either dried in the air and used to prepare an oil-gas, or they are more profitably treated to recover the fat, which is a separate part of the treatment of the suds. It may be undertaken by large mills and wool-washing establishments; smaller works find it more advantageous to sell the press-cakes to the grease-extractors.

In recovering the fat, the press-cakes are stirred with very dilute hydrochloric acid to a thin paste: if necessary, more hydrochloric acid is added to produce a weak acid reaction. The mass is then forced through a filter-press heated by steam. The fat and the reformed calcium chloride run into small vats, from which, after some time, the calcium chloride solution, containing excess of hydrochloric acid, is drawn off into a vat containing carbonate of lime, which on neutralizing the hydrochloric acid again produces calcium chloride, and this is used to produce fresh quantities of lime soaps. Thus it is only requisite to procure a supply of calcium chloride once for all. The fat is heated in a pan over an open fire to 70° C. with 10 per cent of sulphuric acid of 10° B.; after standing some time it forms a clear layer on the top, which is skimmed off into barrels, and is then ready for sale.

Treatment of Wool-washing Waters with Baryta.—Daudenart and Verbert, of Schaerbeek, near Brussels,¹

¹ "Deutsche Industrie-Zeit."

mix a solution of barium chloride in a closed vessel with magnesium carbonate, carbon dioxide being at the same time introduced; barium carbonate is then obtained. The magnesium chloride, which remains in solution, is converted by superheated steam into hydrated magnesia, when hydrochloric acid is obtained as a by-product. This process is designed for the utilization of wool-washing waters, which are mixed with baryta solution, the precipitate pressed and decomposed with hot dilute hydrochloric acid. The separated fat is skimmed off, the liquid evaporated, and the residue of barium chloride converted into barium carbonate by the method described above.

The liquid from which the barium soap has been removed is evaporated to dryness, the residue, consisting mainly of potash, is calcined, and converted into refined potassium carbonate in the usual manner.

Utilization of the Residues of Wool-washing.—Into the fatty waters, which are contained in large masonry tanks, sulphurous acid enters direct from the furnaces in which the sulphur or pyrites is burnt.¹ After the mass has become acid, it is allowed to stand for twenty-four hours. The tank then contains three separate layers—the uppermost consisting of impure fat, the bottom of an earthy deposit, whilst the middle layer contains the sulphites of soda, potash, and ammonia. This middle layer is concentrated by evaporation, and the residue burnt in a furnace. The sulphites are then converted into sulphates, which are obtained by solution and crystallization. The upper layer is heated and pressed in bags, in order to obtain the fatty acids.

A. Gawalowski, of Brünn, has obtained a patent for a process for the recovery of the *fat from wool-scouring waters*, and other industrial waste waters containing soap. The essential features of this process are: Sulphurization of the suds and acidification; the sulphuretted hydrogen, at the moment of its production, acts on the resulting scum, destroying the aniline dyes to a great extent. The decanted scum

¹ Chaudet, "Muster-Zeit.," 1873.

is impregnated with chromates, by which the size, starch, and dextrine are partially oxidized; this process takes place slowly, but is more complete on standing. The scum, after this treatment, is washed, by which the dyes, the oxidized mineral pigment, and also the gluten and oxalate products are removed. The wash water is deep red to brown. At the same time, the scum, already oily, can be kneaded in water like butter or lard, but can no longer be mixed with it to a liquid similar to the original suds. It still contains an excess of chromates and traces of free acid, and would therefore easily destroy press cloth. Gawalowski accordingly stirs it with a reducing solution, which changes the chromate to chromium oxide, and then presses out the neutral green liquid in the cold, after which the cake of scum is pressed warm. This method of treatment results in the highest yield of fat being obtained, a purer product moreover, which can well be used, after the acid has been removed, in spinning dark coarse yarn.

In the Yorkshire district¹ the wool-scouring liquors are run into a large brick-lined tank, in which they are treated with a sufficiency of oil of vitriol diluted with water to render them slightly acid. From the first tank the mixture runs into a second where the grease rises to the surface in the form of a scum, the liquid is filtered through coarse clinker in the bottom of the tank, the grease remaining on the surface being scraped off and wrapped in squares of canvas which are then hot pressed in a hydraulic press at 400-500 lb. pressure per square inch. The grease runs through the bags into tanks or barrels placed below. It is a brown solid grease melting at about 105° F. and worth from £8 to £12 per ton. It is used in very large quantities in the woollen districts for working up shoddy and mungo. The liquid from the tanks is sufficiently pure to turn into the streams. Most manufacturers are averse to treating their waters, but where it has been done there is a considerable profit. The grease is also distilled with superheated steam yielding "distilled grease

¹"The Wool Year Book," 1914, p. 252.

oleine" and "distilled grease stearine," both of which are valuable products, the former being employed for oiling wool, and the latter as a sizing tallow. The following is an analysis of recovered or Yorkshire grease by Lewkowitsch:—

Volatile acids	1.28
Insoluble free fatty acids	20.22
Combined fatty acids	48.47
Alcohols	36.47
	<hr/>
	106.44

The excess over 100 in this analysis is due to the water taken up by the fatty acid and alcoholic radicles as a result of the hydrolysis. The alcohols are cholesterol and iso-cholesterol principally.

CHAPTER XIX.

COTTON-SPINNERS' WASTE.

COTTON waste ¹ consists of soft waste and hard waste. The former, being the waste from opening and carding machines, is in an open condition, the latter is from the spinning frames, cop bottoms, etc., and is more or less twisted.

The soft waste is moderately easy to treat, being worked up in a similar manner to ordinary cotton and spun for the manufacture of sheetings, flannelettes, towels, and quilts, or it is converted into wadding, and also into gun-cotton. In the manufacture of wadding it is put through a wadding plant consisting of carding engine, travelling chain creeper, lap-forming apparatus, gumming machine, and drying chest.

The hard waste requires stronger treatment, being put through a waste machine consisting of an iron cylinder provided with strong steel teeth and an iron doffer similarly provided which opens out the waste; after which it passes through a breaker and a scutcher which cleans it and forms it into a uniform lap, which passes to the carding engine, Derby doubler, a second carding engine, and then to the mule or ring-spinning machine.

Waste which is too hard spun to be utilized by either of the above methods is opened up by means of a very powerful opening machine and is then sold as engine-cleaning waste. As previously mentioned, this waste, even after use, is still valuable, being treated for the extraction of the oil and then again used for a similar purpose.

Cotton-spinners' Waste in the Manufacture of Gun-cotton.—According to the English patent of Mackie, the waste of cotton-spinning is treated with superheated steam

¹ See "The Cotton Year Book," 1914, p. 232.

in order to remove the oil, then carded and immersed in the usual acid mixture—300 parts of a mixture of 1 part of nitric acid (specific gravity, 1.52) and 3 parts of sulphuric acid (1.85), cooled to 5-25° C. The guncotton produced is carefully washed, cut to pieces by means of a rapidly rotating circular knife, and finally passed between rollers, from which it issues in a very finely divided state. This cutting and squeezing are said to have the advantage over the usual pulping in the beating machine, in that all the capillary tubes are completely destroyed, and thus any residual acid can readily be washed out.

The succeeding operations consist in mixing the nitrated cotton with saltpetre and sugar (67 parts of guncotton, 28 parts of sugar, and 5 parts of saltpetre), granulating the mixture by means of wire sieves, and drying in tightly closed pans heated to about 38° C., in which a vacuum is maintained by a pump. An increased addition of sugar and saltpetre decreases the violence of the explosion of the guncotton.

According to the English patent of J. Hall, rags and other linen waste are brought into a bath composed of equal volumes of nitric acid (specific gravity, 1.5) and sulphuric acid (specific gravity, 1.84), and diligently stirred in it for 12-24 hours. The mass is then allowed to drain, pressed, carefully washed for 7-14 days, and dried. For purposes for which a violent explosion is not required, the guncotton, whilst still moist, is mixed with starch paste.

Heddebault has discovered a method by which wool can be removed in the dissolved state from fabrics in which it is contained in admixture with cotton or other vegetable fibres. When these fabrics are subjected to the action of superheated steam under a pressure of five atmospheres, the wool dissolves, and falls to the bottom of the vessel, whilst the cotton, flax, or other plant fibre resists the action, remaining in a condition suitable for the manufacture of paper. The fluid mass, in which the dissolved wool is contained, is evaporated to dryness; it is completely soluble in water. Rags treated in this manner gain in value to a sufficient extent to cover the cost of the process.

CHAPTER XX.

JUTE WASTE.

Treatment.—The softening, beating, and carding machines are used in treating jute waste.¹

1. *Jute Cord and Fabric.*—Both these are collected and go into the store as the first waste product. The latter is used for packing purposes. The former is first unknotted by hand-labour outside the factory, then untwisted or unravelled, and cut into lengths of about a yard, which are laid parallel to one another, made up into bundles of about 45 lb., and tied together. A large number of these bundles go into the softening house, where they are sprinkled with water and fish oil or mineral oil emulsion, allowed to lie in layers, and then taken to the breaker card. The jute cord is treated either alone or mixed with other jute.

2. *The root ends*, which have been cut off, are worked up in the same manner as the cord into the lowest yarn numbers, and are spread out on the feeding-table of the corresponding breaker card. Other waste, which is formed at times, is, instead, taken to the finisher card, which treats the corresponding qualities. In order that markedly different slivers may not be produced by too rapid supply, these tow slivers must be introduced slowly and as thin as possible over the feeding-rollers. The moment of passing the rollers is the best for adding faulty slivers.

3. (a) *Carding Tow.*—In the first place, the shorter strips of fibre are sorted out by hand, and again subjected to the carding operation, after which they are given a beating or shaking treatment. The lower qualities of this tow are sepa-

¹ E. Pfahl, "Dingler's Journ.," 222, p. 573.

rately collected and stored in suitable places in the open; they are removed by cartloads for manure. The better qualities are compressed in box-presses to bales weighing 2-4 cwt., which are tied up and sold to paper or pasteboard makers.

(b) *Spinning Tow* is not subjected to a special treatment; either alone or mixed in the shaking machine with the breaker tow, it is pressed into bales, packed, and sold to papermakers.

(c) *Roving Tow* can be readily introduced into the spinning process. It is either placed on the cloth of the breaker card together with long jute, or, preferably, it is passed through the softening machine, and then taken to the finisher card for further treatment, for which purpose this machine must be supplied with a feed-table, the fibres thus produced being longer. The roving tow should, however, never be added for re-treatment to medium or better qualities.

(d) *Good Tow from the Fine-spinning*.—The dropped threads of the rovings are sorted, mixed with the roving tow, and spun together with it. A second sorting of the tow then takes place in the softening house, after which it is sent once through the softening machine and then over the tow carder, when a loose and very soft cleaning material is obtained, which is packed in sacks, or, better, compressed into bales, and sold to railway workshops, etc. This tow is not suitable for spinning.

(e) *Clean Thread Waste*.—This is passed once or twice through the softening machine, when it also gives a very fine cleaning material, which, however, is somewhat less soft than the preceding substance. The waste, after this treatment, is frequently used for stuffing ordinary mattresses, sofas, etc., in place of flax tow, in comparison with which it has the advantages of cleanness and purity, but it has, however, the smell of fish oil.

(f) *Ordinary Sweepings*.—From the sweepings any good waste, such as sliver, roving tow, etc., is sorted out; then follows the search for oily cleaning waste, which, owing to

the presence of oil is regarded as liable to produce danger by fire, is sent to light the fires in the boilerhouse, for which no better utilization can be found. The remainder is either at once mixed with the beating ordinary carding-tow, or is previously beaten, when the better-class fibres remaining in the machine are united with the tow from the breaker card.

The tow-cleaning machines may be divided, according to the nature of the beating apparatus, into (a) simple beating or shaking machines, (b) conical shaking machines, and (c) double shaking machines. Of these three machines, the most practical are the first and last.

Simple Beating or Shaking Machine.—In a cylindrical vessel, the upper half of which consists of a tight casing with a door for admitting and removing the material, and the lower half a grating of laths, moves a horizontal shaft provided with fast and loose pulleys. On the shaft are found six series of round iron rods as beaters. As the shaft rotates, the beaters move between two other series of fixed rods. The side walls of the machine are well boarded, so that the dust-chamber is formed under the grating. After the waste (carding tow) has been introduced through the above-mentioned door, and distributed throughout the machine, the door is closed, the shaft set in motion, and the beating operation allowed to proceed for 10-15 minutes. The shaft with the beaters is then removed, and the machine emptied of the cleansed waste through the door. The dust, sand, bast particles, etc., beaten out, fall through the grate into the dust-chamber. They are most readily and conveniently removed from the workroom if the machine is erected over a brickwork pit, connected by means of a passage with a special dust-shed in the open. If the drainage conditions do not permit such a pit and connection with a shed, the shaking machine must be erected in an elevated position, a large box running on wheels being brought under the dust-chamber, in which the ordinary refuse shaken out can collect. If the dust-chamber is connected with a fan which carries away the lighter dust to deposit it in a suitable position, it is still necessary to have an arrangement of this kind for collecting

the heavy particles. The beater-shaft usually has a speed of 260-280 revolutions per minute.

Double Beating Machine. Two horizontal shafts, each with six series of iron beaters, are so arranged in a cylindrical casing that the rods of one move through the spaces between the rods of the other. The casing also in this machine consists of an upper tight cover and a grating below. The beaters in addition strike through another series of rods. The opening for charging is closed by a counterpoised door during use. The dust-chamber communicates either with a pit or with a closed box; a fan may also be used. The feed is fixed in the upper part of the cover; it consists of an endless cloth, a small loose roller, and a roller, studded with needles, moving at a high speed—both in a tight-fitting casing. The needle roller is designed to introduce the material, as far as possible, into the beater in an unravelled and divided state. A certain quantity of waste is brought into the machine and the feed set in motion. In a few minutes the door is opened, so that the cleaned material may be thrown out and caught in a box placed to receive it. The door is then closed and a fresh quantity introduced. This repeated change can readily be worked automatically by suitable mechanism.

The Tow Carding Machine or Teaser Card. A rotating drum, to which the material is brought by the feeding apron and grooved rollers, is surrounded on the upper half by three pairs of turning and squeezing rollers working together. These rollers treat the material in the known manner; it then goes to the delivery roller, from which it is drawn off by smooth rollers as a coherent fleece and carried on to the delivery apron. The machine is therefore a semi-circular card, with an upper working half. In order to prevent the production of dust, the rollers are all protected by a sheet-iron cover. The diameter of the drum is generally 3-4 feet; it is about the same in length, and runs at 100-120 revolutions per minute. The rollers move at various velocities, which have to be adjusted to the needs of the moment. The ratio of the velocity of feed to that of delivery should be at the most 1 : 15.

CHAPTER XXI.

UTILIZATION OF RAGS.

A VERY large quantity of rags of various kinds are collected from ashpits, and from the marine store dealers. These rags are sorted into different heaps according to the nature of the fibre and their colour. Woollen rags, as before stated, are used in the manufacture of shoddy and mungo; cotton and linen rags go to the papermaker; silk rags to the manufacturer; while old rope and string, old canvas bags, etc., are all utilized in some way or another.

Woollen rags or cuttings are also made into carpets. For this purpose they are cut into strips about $\frac{3}{4}$ in. wide and 6-8 ins. long, and drawn through a piece of coarse canvas or hessian so that both ends are on the same side. Simple patterns are made with rags of different colours. These carpets are very warm and durable, and, owing to their cheapness, are eminently suited for kitchens. Printed cotton and silk cuttings are cut into various patterns and stitched together to form quilts and bedcovers. Both these were home industries at one time, but the modern tendency of buying everything ready made is gradually replacing them by factory-made goods which though more showy are not necessarily more durable.

CHAPTER XXII.

COLOURING MATTERS FROM WASTE.

Utilization of the Waste from Dye-wood Extracts.—Croissant and Bretonière, of Laval, gave a detailed account of their work in this direction in 1875.¹ In the first place, this concerns the solid dye-wood extracts, each of which contains its own peculiar tannin or colouring matter. Now gallic acid, a product of the decomposition of tannic acid, on heating to about 250° C., gives metagallic acid. The chemists named therefore treated logwood extract by the same reaction, when they obtained an evolution of carbon dioxide and a black voluminous substance, insoluble in water, but readily soluble in alkalis, and precipitated from these solutions by acids in the form of brown flocks. With solutions of different metallic salts it gave variously coloured precipitates. This decomposition of logwood extract, accompanied by the evolution of carbonic acid gas, also takes place at 200° C. in the presence of caustic alkalis. In the latter case is obtained the soluble alkali salt of an acid analogous to metagallic acid, which is precipitated from its solutions on the addition of other acids or of metallic salts. One important point is that the alkaline solution of this compound has a very strong direct dyeing power for vegetable fibres. If instead of the natural colouring matters the same process is applied to other organic substances, there is known to result by the action of alkalis a salt of oxalic acid, e.g. from sawdust. The reaction, however, takes quite a different course if sulphur be at the same time introduced into the compounds. Either the sulphur enters into direct combination with the substance without

¹ Bull. Soc. Ind. Mulhouse; "Dingler's Journ.," 215, p. 363.

the elimination of any element, as in the case of the aloe, or, as more frequently happens, the sulphur unites with a portion of the hydrogen of the organic substance to form sulphuretted hydrogen, which is volatilized, the organic substance thus becoming reduced. In both cases, however, and from many organic materials, there are produced in this manner new substances, which act as substantive dye-stuffs for animal and vegetable fibres, which produce intense and fast shades without the assistance of a mordant.

The discoverers have heated a series of the most diverse organic substances in closed vessels with sodium mono- and poly-sulphide, and in every case find confirmed the correctness and general applicability of their discovery.

The colouring matters are readily and certainly produced in the form of a swollen voluminous mass, more or less dark in colour according to whether the temperature of preparation was higher or lower, between the limits of 200-300° C., and according to the longer or shorter duration of the heating. The solubility of the product also increases with the temperature and duration of heating, as also the fastness of the effects produced on fibres, especially in regard to the action of light. All the products are very hygroscopic, and therefore require to be kept in well-closed sheet-iron boxes; it is also necessary to guard against oxidation by the air, by the action of which the colouring matter is converted into an insoluble substance. Without this precaution they become quite useless in four to five months. In a freshly prepared dye-bath the colouring matter has such affinity for vegetable and animal fibres that, when the dyeing is sufficiently protracted, the whole may be withdrawn from the bath and a colourless liquid left. Of particular importance to the productiveness of this colouring matter is the nature of the water employed. In waters containing lime it dissolves only incompletely; if only such water is available it requires to be purified before use by boiling with soda. The colouring matter is also separated from its solution by acids, but the precipitate readily redissolves in dilute alkaline liquids. This behaviour affords a

means of purifying the colouring matter, and obtaining it in the form of a dry unalterable powder, soluble in alkaline liquids. Other precipitants are alum and metallic salts; the precipitates vary in colour according to the metal contained in the salt. The most useful precipitant for dyeing purposes, however, is potassium bichromate, owing to the oxidizing action of the chromic acid it contains, and because the precipitates which it produces, with few exceptions, are quite unacted upon by most solvents, even by boiling caustic liquors; therefore this salt is a most valuable means for fixing the colour upon the yarn or fabric.

CHAPTER XXIII.

RESIDUES IN THE MANUFACTURE OF ANILINE DYES.

Utilization of the Residues.—In the manufacture of magenta, resinous residues are produced, which contain, in addition to organic matter, almost the whole of the arsenic originally employed.

According to Bersch, this arsenic may be regained by various methods. The arsenious and arsenic acids in the residues are first brought into solution by boiling with hydrochloric acid, and extracting the undissolved residue with water. The two solutions are mixed and neutralized with soda, when a dark green precipitate is produced. The liquid filtered from the precipitate, consisting of a solution of sodium arsenite and arsenate, is mixed with milk of lime, which precipitates calcium arsenate. The precipitate is decomposed in lead-lined vats by means of sulphuric acid, to which a little nitric acid has been added. The solution of arsenic acid is drawn off from the deposited sulphate of lime and again used, after concentration, for the oxidation of aniline oil.)

In order to work up the mother liquors of the magenta manufacture for arsenic acid, the acids of arsenic are precipitated by lime, the precipitate washed and dried, and the arsenic reduced by ignition with coal. The arsenic vapours evolved are allowed to come in contact with hot air, by which they are burnt to arsenious acid, which is condensed, and again oxidized by nitric acid to arsenic acid. This process is, however, only suitable if concentrated liquors are in question. Weak liquors have to be evaporated in shallow pans, which are heated by the flue gases from other ap-

paratus; after this concentration they are treated by the former process.

Another method, which (according to Bersch) is suitable for works where very cheap fuel is obtainable and for working on a very large scale, consists in mixing the very concentrated solution of sodium arsenate with powdered chalk and lignite, drying, and heating the mass in a furnace. The vapours of the (reduced) arsenic passing from the furnace are, by contact with the air, burnt to arsenic trioxide, which is condensed and deposited in long flues. The residue in the furnace consisting of soda mixed with calcium carbonate is extracted with water; thus the two substances are separated, to be again used in succeeding operations for recovering arsenic.

In order to obtain magenta from the mother liquors left after the crystallization of the dye-stuff, soda solution is added to them, which separates the magenta base. From the residual liquid the arsenic is regained by one of the methods described.

When the mother liquors are worked up systematically, shallow leaden pans are employed, these being closed and provided with vapour pipes leading into a chimney with a good draught. When possible, the pans are heated by the flue gases from the vessel in which aniline is transformed into magenta. The very concentrated mother liquors yield a considerable quantity of sodium arsenate, and the liquid still remaining may, in order to obtain the rest of the arsenic, be precipitated with lime, and the precipitate converted into arsenic acid; as previously described.

By systematic treatment of the impure mother liquors from the manufacture of magenta, several firms have succeeded in producing certain definite shades of reddish-brown and brownish-red, passing into the deepest brown. It is of the first importance always to produce these of the same nature, so that the same shade of colour may always be produced by a dye which has once been known in commerce under a certain name. This object may be attained, accord-

ing to Bersch, by always working by one and the same process in the manufacture of magenta, and by always treating the mother liquors by the same process of evaporation.

Treatment of the Residues produced in the Manufacture of Aniline Red.—The methods with arsenic acid and mercuric nitrate, as also Coupier's process with nitrobenzene, iron, and hydrochloric acid, give only a yield of 30-40 per cent of the aniline employed in the manufacture as saleable dye. The Actiengesellschaft für Anilin-Fabrikation, of Berlin, has now found, according to a patented process, that the air-dried residues give, on dry distillation from horizontal retorts, a distillate which, together with water and ammonia, also contains aniline, toluidine, xylydine, and their homologues, which can again be directly employed in the manufacture of aniline red; in addition to this there is produced a high-boiling oil, consisting principally of diphenylamine, but containing also naphthylamine and acridine. The residual coke is used as fuel.

Treating with a Solvent Waste Acids from Nitrations.—No. 15,455 of 1915.—J. W. Leitch, B.Sc., of Somerville, Edgerton, Huddersfield, claims: (1) A process of continuously extracting by means of solvent nitro-compounds from waste acids from nitration by running together in suitable proportions the solvent and acid into a mixing vessel while maintaining the conditions of temperature and concentration suitable for the extraction, and allowing the mixture to flow into settling tanks from the vessel through an overflow pipe. (2) The apparatus for the process referred to in claim 1, comprising a closed vessel containing a vertical stirring shaft having propeller blades, surrounded in known manner by a cylinder open at each end, these blades being adapted to draw the liquid upwards into the sphere of action of other propeller blades on the shaft which throw the liquid outwardly and downwardly, the cover of the vessel having a trough for distributing the liquid continuously charged into the vessel, an overflow pipe to the vessel for continuously discharging the liquid to settling vessels, and devices for internally or externally heating or cooling the vessel.

CHAPTER XXIV.

DYERS' WASTE WATERS.

Recovery of Arsenates and Phosphates.—For the recovery of arsenates and phosphates from the solutions used in fixing the mordants—the so-called “dunging”—the following process has been patented by Higgins and Stenhouse: The waste liquors are mixed with an iron or manganese salt, the mixture made alkaline by milk of lime, and allowed to settle. The precipitate, which contains the arsenic and phosphorus, after removal of the clear liquid, is brought on to cloth strainers. A portion is examined for the percentage of bases it contains, and an equivalent quantity of sodium monosulphide added to the whole bulk. The mixture is then boiled with water in a steam-jacketed pan for two hours. The resulting clear solution contains sodium arsenite, arsenate, and phosphate; if a little sodium sulphide should be present, it is oxidized by means of sodium hypochlorite. The solution is now again available for “dunging,” but if it should be found too alkaline it is neutralized by a mineral acid.

Recovery of Dyes from the Waste Liquors.—This patented discovery is due to Remmers, of Glasgow. It accomplishes the recovery of alizarine and purpurine from the waste liquors obtained in dyeing Turkey reds and other shades, for which madder or artificial alizarine is employed. For this purpose the waste liquors are run into a large tank, into which hydrochloric or sulphuric acid is run in quantity sufficient to precipitate the whole of the colouring matter from the solution. The reaction is accelerated by stirring. After settling, the clear liquid is drawn off from the precipitate, the

latter being boiled for some minutes, when necessary, with a little acid, until the liquid acquires a yellow colour. After cooling, the precipitate is separated from the liquid by means of a filter press, and washed until neutral, when it may again be used in the same way as the original material.

Recovery of Tin from the Waste Waters of Dyeworks.—Mogret has given an account of the recovery of tin from the waste liquors of dyeworks.¹ To a greater extent than ever, tin preparations, in the form of stannic or stannous salts, play an important part in dyeing, both as mordants and for weighting silk. Hardly half the quantity of tin used is really utilized, the other half being lost in the used mordanting or dyeing baths or in the wash waters of yarns and fabrics. Since this metal is expensive, the wash waters and used liquors represent a considerable sum. In order to regain a portion of the valuable constituents, which run into the drains and contaminate the rivers, the dye-baths and wash waters are collected in tanks. In these the tin is precipitated by the addition of granulated zinc, or, better, of zinc dust—known under the name of “preparation”. The precipitated tin, mixed with stannic oxide, is filtered through woollen cloth, the precipitate washed, dried, and melted at a white heat, with the addition of borax and a little granulated zinc. The stannic oxide is reduced to metal by the zinc, the excess of zinc being volatilized at the high temperature employed. In this manner pure metallic tin is obtained, which is poured into moulds, and is of considerably higher value than the zinc used in its recovery. This method is said to be employed in several large works in France.

With regard to dyers' waste waters generally, they are, whenever convenient, turned into the nearest stream or river. This is, however, not always possible, besides which it is never desirable to turn out impure liquids in this way. In some works large brick tanks are constructed into which the liquors are run. Acid liquids are neutralized with lime or alkaline liquids with sulphuric acid, in some cases with de-

¹ “*Moniteur de la Teinture*,” 1889; “*Färber-Zeit.*,” 1889.

position of the colouring matters. Sometimes dyes mutually precipitate each other. After standing, the liquid is passed through sand filters or bacteria beds and is then sufficiently pure to be run into a stream. Alkaline bleaching liquids are purified by the septic or closed tank treatment and then passed through sand or coke.

CHAPTER XXV.

WASTE PRODUCED IN BUTTER-MAKING.

IN creameries where butter is produced the cream is separated from fresh milk by centrifugal means more completely than can be done by hand, and is either sold in that state or converted into butter. This leaves as a residue a considerable proportion of skim milk containing only about 0·3 per cent of fat. The following analyses show the composition of whole and skim milk :—

	Whole Milk.	Skim Milk.] . .
Fat	3·50	0·46
Casein and albumin	4·75	3·37
Sugar	4·17	5·34
Ash	0·70	0·72
Water	86·88	90·11
	100·00	100·00

Several methods of utilizing this skim milk have been devised. In Ireland a considerable proportion of it is converted into condensed skim milk, for which purpose it is evaporated in a vacuum pan at 100-120° F. until sufficiently concentrated and the requisite quantity of sugar added.

The composition of such milk is as follows (Dold & Garratt):—

Fat	0·78
Casein, etc.	10·33
Ash	2·16
Cane sugar	50·35
Milk sugar	10·92
Water	25·46
	100·00

This condensed skim milk is a useful article of diet, particularly where cheapness is important, but, as pointed out by

many medical men, it is not at all suitable for infant feeding owing to its deficiency in fat.

The skim milk has also in America been converted into cheese, and although such cheese may not be easily digestible, its sale is quite legitimate provided that it is labelled in a proper manner. Certain manufacturers of this commodity were at one time not content with this, but replaced the butter fat with margarine or lard, and sent it to this country to pass muster as genuine cheese and thus command a higher price.

A proportion of the skim milk is treated for the separation of casein. For this purpose it is slightly acidified or treated with rennet, the curd which separates being washed to free it from soluble impurities and then dried by centrifugal means, followed by hot air with or without a partial vacuum. The casein thus produced forms a very light flocculent powder which is easily dissolved, or rendered fluid by ammonia or borax, the paste thus formed being used as an adhesive also in the dressing of cloth and surfacing of paper. Casein is also mixed with zinc oxide and other pigments and moulded into various articles. This is known as galalith, etc. Some of these products resemble natural ivory so closely as to be with difficulty distinguished from it.

Another use for casein is as a food product. It is highly nitrogenous and is a valuable dietetic substance. It is mixed with flour and made into biscuits, also with cocoa, etc. A well-known blood enricher is also casein in an almost pure condition.¹

The liquid or whey drained from the casein contains the milk sugar. The following is an analysis of such whey :

Fat	0 10
Proteids	0·27
Milk sugar	3 05
Ash	0·47
Water	94·11

100·00

¹ "Casein: its Preparation and Technical Utilization," by Robert Scherer.

For the separation of the milk sugar it is necessary that the whey should be fresh, as fermentation destroys it, yielding lactic acid, alcohol, etc.

The whey is neutralized and evaporated considerably when impure milk sugar separates in hard crystals. These are dissolved in water, purified by passing through animal charcoal, and the solution again evaporated, yielding practically pure milk sugar. The sugar thus produced has the same composition as cane sugar ($C_{12}H_{22}O_{11}$), but quite different properties, for instance it is scarcely sweet. It differs also from glucose or grape sugar. It is used principally for adding to cow's milk for making "humanized" milk, also for the preparation of lozenges and medical tablets, for which purpose it is eminently well fitted.

CHAPTER XXVI.

MOLASSES.

Utilization of Molasses.—One of the uses of molasses is in the manufacture of spirit. For this purpose its value depends on the percentage of sugar: in order to estimate the value the molasses are diluted, say to 18° on an ordinary saccharometer, the solution mixed with an excess of yeast at 24-25° C., brought into a warm place, and allowed to ferment. If now the saccharometer shows 3° unfermented, there was in the 18° solution apparently (since the spirit present in the fermented liquid affects the saccharometer reading) 15° of sugar; thus in molasses which showed 45° originally, 37·5°. In order to find the true amount of sugar, the fermented liquid is boiled, the alcohol driven off, and the loss in boiling replaced by distilled water; a polariscope reading is again taken, when the percentage of sugar indicated by the instrument is the true unfermented. For example, if the saccharometer shows 19° before fermentation, in the unboiled fermented liquid 4°, in the boiled fermented 5½°, then there are really 13½° fermentable.¹

Usually, however, the percentage of crystallizable and uncrystallizable sugar are determined by means of the polariscope and Fehling's solution.

Molasses contain sugar, salts, nitrogenous and nitrogen-free compounds, alkalies, and alkaline earths. The latter hinder fermentation. In order to neutralize the alkalinity which retards fermentation, 0·5-1·5 per cent of sulphuric acid, as required, is added to the molasses. Molasses do not need mashing, but they are somewhat diluted in the mash-tun, ac-

¹“Populäres Handbuch der Spiritus- und Presshefe-Fabrikation,” A. Schönberg, 4th ed., Vienna, Hartleben.

ording to their thickness, and the sulphuric acid, previously mixed with water, added. The mixture is then heated until the sour-smell disappears. Acid is only to be used when the molasses have an alkaline reaction; if this be the case, acid is added until blue litmus paper dipped in it is coloured a weak wine-red. It is preferable to add the water in the mash-tun, and to prepare the liquid there, for if the water is added in the fermenting vat there is difficulty in stirring the liquid. The molasses is intimately mixed with the water; and since cold molasses mix with water with great difficulty, heat is applied whilst mixing in the mash-tun. A cooler is necessary in molasses works. Whether sulphuric or hydrochloric acid is employed for neutralizing depends on the success with which the liquid ferments. Generally, after neutralization with sulphuric acid, 1-2 lb. of hydrochloric acid are added to a tun containing 90-100 buckets (say 300 gals.). Many samples of molasses require no hydrochloric acid; those which require it are generally the produce of works using beet from wet, heavy soil, or from uncultivated ground. As a rule, the quantity of hydrochloric acid is 5-10 per cent of that of the sulphuric acid.

An intense green malt yeast is generally used for molasses wort, to which beer yeast or pressed yeast is added every day, since molasses worts require a very heavy fermentation; 10 per cent of yeast is employed as a rule. It is also very advantageous to initiate a very strong preliminary fermentation. The wort after adding the yeast soon acquires a layer on the top 3-4 ins. thick, below which, if the treatment has been successful, a very intense fermentation proceeds. The fermenting vessels are filled to within 2-3 ins. of the top, and the wort pitched at 30-44° C.

If beet juice is available, it is used for diluting the molasses. If a vat does not commence fermentation properly it is assisted by an addition of beer yeast or fermenting wort. Care has to be taken that the fermenting room is always at a temperature of 18-20° C. Since these worts rapidly cool and ferment with difficulty, it is necessary to have one

or two stoves in the room, so that it can be warmed during the winter months.

After distillation the spent wash of country distilleries is used as food for cattle, mixed with more or less other materials; it is also used as manure. In large distilleries the wash is evaporated in the "thickening pans," and then brought into calcining furnaces built like black-ash furnaces. As a rule three furnaces are arranged in steps—one below the other; as the wash becomes concentrated it is allowed to flow from one to the other, being carbonized in the last. According to the quality of the molasses, 11-12 per cent of carbonaceous residue is obtained, containing about 50 per cent of potassium carbonate. The free acid in the wash is frequently neutralized with lime, the sulphate of lime is then allowed to deposit, and the wash, after evaporation in the pans, brought into the above-mentioned calcining furnace in order to destroy the organic matter.

When given in large quantities to cattle, molasses wash causes sickness.

If potatoes are to be worked together with molasses, it is most convenient to mash the two together, and to mix them in the inverting vessel. The prepared molasses wort is run into the inverting vessel during the grinding of the potatoes. If, however, there is no vessel in which the molasses wort can be made, it is done in the inverting vessel, and the ground potatoes added. The best proportion is 25 cwt. of potatoes to 2.5-3 cwt. of molasses of 42°. The manipulation is the same as with potato worts, except that the yeast must be increased in proportion to the molasses. With these proportions the wash may be used as fodder without fear.

C. Vincent has introduced a *process for the more rational utilization of vinasse—the residue left after distilling the alcohol from fermented beet molasses* ("Chemical News"). Formerly the vinasse was calcined in open hearth furnaces for the recovery of the potash salts. The idea of utilizing the gaseous compounds produced in this process had been mooted years ago, but has only recently been realized by

Vincent. In this process the calcination is performed in cast-iron retorts; the products of distillation, which condense at the ordinary temperature (tar and ammonia water), are caught, whilst the gaseous products are led away to heat the retorts. The ammonia water is practically similar to that obtained in making gas by the dry distillation of coal, but contains, in addition to the ordinary constituents, methyl alcohol, methyl cyanide, methyl sulphide, and, what is particularly remarkable, a large quantity of trimethylamine salts.

The aqueous alkaline product of the distillation is, according to a further account in the "Pharmaceutische Zeitung," first over-neutralized with sulphuric acid and then distilled. Methyl alcohol comes over; on cooling, ammonium sulphate crystallizes from the residue. The mother liquor contains much trimethylamine sulphate.

Trimethylamine has at present no particular commercial value; it is, however, very suitable for the production of methyl chloride. When trimethylamine hydrochloride is heated, it decomposes into ammonia, free trimethylamine, and methyl chloride. The decomposition begins when the boiling point of the concentrated mother liquor of the trimethylamine salt has reached 260° C., and is complete at 325° C. The gaseous products are conducted through hydrochloric acid, which retains the alkaline compounds; after sal-ammoniac has been separated from this solution by evaporation and recrystallization, the solution is again subjected to distillation. The methyl chloride which passes over, after purification by washing with dilute caustic soda solution, is dried by strong sulphuric acid, and pumped into iron or copper cylinders closed by screw-cocks. The gas is liquefied by pressure in these cylinders, in which state it is sold.

Methyl chloride has two technical applications; it is very suitable for the production of "artificial cold," and it is used in manufacturing methylated aniline dye-stuffs, which have previously been very costly owing to the use of methyl iodide. When methyl chloride evaporates, its temperature falls to -13° C.; but if the rate of evaporation be increased by the

passage of a current of dry air, the temperature sinks to -55° C. Methyl chloride is thus an excellent material for ice-machines.

At the large distillery of Tilloy, Delaume & Co., at Courrières, which was managed by Vincent, 90,000 kilos (90 tons) of molasses were treated daily; 25,000 litres (5500 gals.) of pure alcohol of 90° (Gay-Lussac) were obtained, leaving 40 tons of vinasse, which yielded 10,000 kilos (10 tons) of potash salts, and as condensation products, 1600 kilos (32 cwt.) of ammonium sulphate, 100 kilos (2 cwt.) of methyl alcohol, and 1800 kilos (36 cwt.) of concentrated mother liquors, of trimethylamine salts; the vinasse also yielded 4000 kilos (4 tons) of tar, from which 360 kilos ($7\frac{1}{4}$ cwt.) of oil and 2000 kilos (2 tons) of ammonia water were distilled off.

Other Uses of Molasses.—A very considerable amount of molasses is purified and sold as treacle or golden syrup for food purposes. The remainder, especially the crude beet molasses, is an important ingredient in the manufacture of shoe-blackings.

During the last few years a very large trade has been built up in the preparation of cattle foods containing molasses, usually crude beet molasses. This is mixed with various materials, e.g. peat moss, ground hay, etc., and forms an excellent feeding-stuff.

The residues from beet-sugar manufacture are usually sent back to the farmers, but they are sometimes dried for use as cattle food. Two samples of such material, analysed by Smetham, gave the following figures:—

	Dried Beet Pulp.	Beet Fodder (Spanish).
Water	11.80	12.00
Oil	0.88	0.60
Albuminoids	8.75	8.87
Digestible carbohydrates	58.92	61.52
Woody fibre	16.45	10.21
Mineral matters	3.25	6.80
Sand and silica	0.05	0.05
	<hr/>	<hr/>
	100.00	100.00
	<hr/>	<hr/>
Food units	83	85

CHAPTER XXVII.

THE WASTE LIQUIDS FROM SUGAR-WORKS.

Utilization of the Waste Water.—W. Riehn has described a process¹ by means of which it is possible to remove the injurious effects of the waste waters, and to recover them again with little loss, not, indeed, in the form of a potable water, but in such a condition that they give no trouble in the neighbourhood, and are quite suitable to be used over again in the works or elsewhere. In using this process, in order to avoid a false impression of the extent of the purification it affords, it must not be neglected to remove entirely the deposits in the drains and other legacies of the past. The process may be carried out without any considerable outlay, this being covered by the value of the fertilizer obtained, the work being done by the labour of one man, under careful supervision. The purification is said to attain three objects: prevention of conditions dangerous to health, production of a valuable fertilizer, and recovery of the water. In regard to the operations to be performed, the impure waste waters may be divided into—(1) water used for washing the beet, and from the crude juice station; (2) water from the bone-black treatment, and from washing filters and cloths; and (3) condensation and condensed water from boiling the juice.

The condensed water from the steam engines and other apparatus, which is collected separately and carefully, the water from the evaporators, and the waste juice from the filters, do not need special treatment here; they are already employed to the best advantage in any properly conducted works—for feeding the boilers, treating the bone-black,

¹“Dingler’s Polyt. Journ.,” 223, p. 402.

slaking lime, washing—and give rise to no further inconveniences.

1. *Water Used for Washing the Beet, and from the Crude Juice Station.*—The temperature of these liquids in the waste-pipes varies between 18° and 32° C.; their impurities are largely earth, carried in suspension, other dirt and particles of beet, also juice in small quantity, i.e. sugar, salts, etc. The purification of these waters is very simple;



FIG. 15.

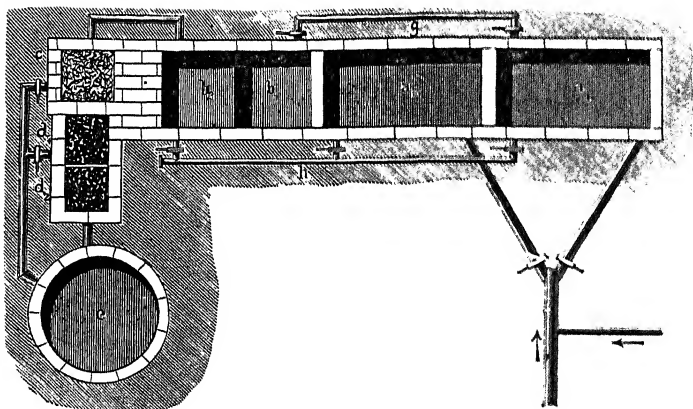


FIG. 16.

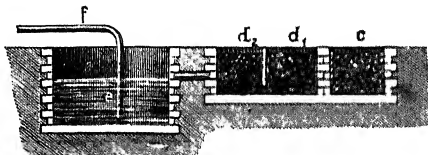


FIG. 17.

the settling-tanks a_1 and a_2 (Figs. 15-17) are quite sufficient for removal of the impurities just mentioned, the small quantities of sugar, etc., being also completely removed by the contents of the filters c , d_1 and d_2 , after the liquid has passed through the tanks and undergone the reactions which

take place there, as described under the next section (2). The water received in the collecting tank e is at least as pure as the original water used, and the necessary cooling has been obtained in the open tanks and conduits. The settling or mud-tanks, a_1 and a_2 , are of masonry, sunk more or less in the ground according to the local conditions; for the daily treatment of 100 tons of beet, each tank is 8·8-9·5 metres (29-31 ft.) long, 3·8-4·4 metres (12·5-14·5 ft.) wide, and 1·9 metre (4·2 ft.) deep. In the case of larger quantities, or very dirty beef, a third such tank is provided. The tanks b_1 and b_2 , also of masonry, are together as large as a_1 or a_2 : they are merely divided by an overflow partition. It is necessary that the valves shown in the figures should be properly arranged, and that all the pipes should have the correct fall. The manipulation is simple: at the commencement all the waste waters run to a_1 , thence through the pipe g to the tank b_1 , etc. When a_1 is filled with deposit the valves are reversed; the waste waters then go to a_2 , whilst a_1 is emptied. From the tanks b_1 or b_2 , in which the last settlings are deposited, the liquid comes to the first filter c , which is 1·9-2·5 metres (6·2-8·2 ft.) square or in diameter, and is the same depth as the previous tanks; it is filled with layers of various grades of cinders, sand, or other material suitable for the complete mechanical purification of the water. The filling material may be suitably mixed with alum mud, iron chloride, potassium permanganate, etc., if such substances are to be obtained cheap in the neighbourhood of the works. From the filter c the water enters the filter d_1 at the bottom, from which it flows over into d_2 (1·6-1·9 metres square or in diameter, i.e. 5·3-6·2 ft.), and finally through a ground pipe into the collecting-tank e (3·2-3·8 metres in diameter, i.e. 10·5-12·5 ft.), whence the purified water is removed to the works by the suction-pipe f .

The contents of the filter are changed as soon as it is so choked that it no longer works. Turf coke is the most suitable filling for d_1 and d_2 ; when it cannot be obtained, waste bone-black is used, or the prepared wood charcoal of Jüne-

mann—charcoal in coarse grains, boiled with a solution of five parts of acid calcium phosphate and five parts of sulphate of alumina, then dried and ignited. This charge is renewed during the season only once, or several times at the most, as soon as the diminished purity of the filtered water makes it necessary. The pipes are laid down in a manner convenient for cleaning, which is necessary only once before and after the season, if they are given sufficient fall. Before the mud-tanks and the filters there is a channel or pipe *h* leading to the tank *e*, and provided with the necessary valves, so that the waters run off direct at the end of the season, or for repairs.

2. *Waters from the Bone-black Treatment, and from Washing Filters and Cloths.*—The purification of these waters offers great difficulties, and the temperature in the waste-pipes varies from 20-60° C.; the quantity and variability of the suspended or dissolved impurities are very considerable. These impurities are organic matters, albumin, alkalies, and alkaline compounds, salts, acids, products of fermentation, etc. A large number of experiments have been conducted to find a universal means for removing these miscellaneous impurities. The author has used turf coke, which is cheap and may be obtained on the large scale by burning in heaps, with the best results for filling the filters *d*₁ and *d*₂. It was found that, by reason of the great porosity and consequent absorptive properties of this material, every trace of sugar, and organic impurities, was removed from the waste waters which passed through. The mineral constituents of the turf coke—iron, gypsum, lime—impart to it even to some extent a disinfecting action; and there is a considerable advantage in that the absorbed matter loses none of its fertilizing value for plants, so that the turf coke, together with these absorbed matters, forms an addition to soil which is most valuable in every respect. In regard to a complete disinfection of these waste waters, according to the author's experiments, only the compound of acid magnesium phosphate with basic iron salt—the double salt of magnesia and iron already re-

commended by Blanchard and Chateau—has been found satisfactory. By means of this compound the whole of the nitrogen is fixed, with formation of ammonium magnesium phosphate; the other organic matters are also precipitated, the sulphur compounds, sulphuretted hydrogen, etc., by the basic iron salt, so that the water is so far prepared for complete purification that, after passing the settling-tank, it only requires filtering through turf coke.

A similar precipitant to Blanchard's—magnesium sul-

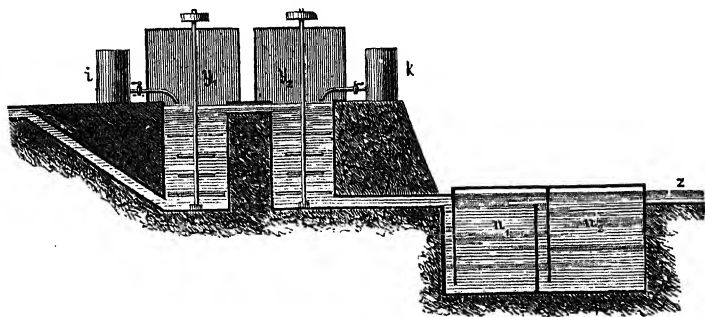


FIG. 18.

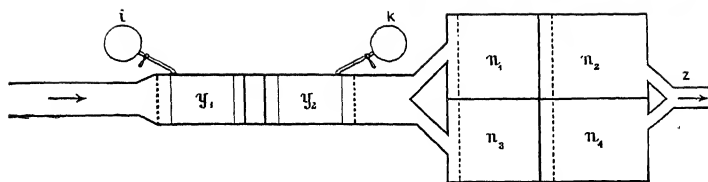


FIG. 19.

phate, calcium phosphate, and ferric phosphate—has also, according to the author, been made for several years by Frank, of Stassfurt, and sold at the very low price of 2s. 6d. per cwt. This preparation is used for the purification under consideration in the following manner: 100 parts are stirred with 66 parts of ordinary hydrochloric acid in a tank or tub and allowed to stand two to three days, 300-400 parts of water are then added. The vessel *i* (Figs. 18 and 19) is filled with this mixture; as much as may be required is run through the exit-pipe into the waste water contained in the first section

of the apparatus y , where it is well mixed by means of the stirrer. Milk of lime from the second vessel k is run into the second section of the apparatus, which is also provided with a stirrer, in sufficient quantity to render the liquid alkaline, so that any free phosphoric acid present may be recovered as tribasic phosphate of lime. The settling of the precipitate, which is generally voluminous, takes place in the sections of the settling-tank n_1n_4 , which are connected together two and two and used in turn. According to the position of the valves, the liquid flows either into the tank n_1 and thence runs over into n_2 , or into n_3 and thence into n_4 . The clarified water then goes through the drain z to the settling-tanks a_1, b_1 , or a_2, b_2 (Figs. 18-19), is mixed with the contents of these tanks, enters into reaction with them, and then runs away for the final purification in the filters, c, d_1, d_2 .

In regard to the construction of this purifying plant, the tanks y_1 and y_2 are built of wooden planks or bricks; they are about 63 cm. (2 ft.) wide and 95 cm. (3 ft.) high, with two divisions, each 63 cm. (2 ft.) long (round or rectangular). The stirrers are driven in the most convenient manner from the nearest shafting. The liquor is fed in at the bottom and runs away at the top; in the hinder wall of each division is a valve just above the bottom for running off the contents. The vessels i and k are of wood or iron, 79 cm. (2 ft. 7 ins.) wide and 95 cm. (3 ft.) high. The settling-tanks n_1-n_4 are of brickwork, open or covered, and connected two and two in such a manner that the water runs over from one into the other; each tank is about 1.3 metres (4 ft. 3 ins.) square and 1.6 metres (5 ft. 6 ins.) deep.

The precipitate collected in the tanks n_1-n_4 possesses great fertilizing value; it has been found by several analyses to contain ammonium magnesium phosphate equivalent to 28 per cent of phosphoric acid and 10 per cent of ammonia, also varying quantities of readily soluble basic phosphate of lime, the sulphur compounds combined by the iron salt, and various nitrogenous and organic substances. Together with the deposits in the settling-tanks and the contents of the filters, it

produces an excellent fertilizer, the value of which covers all expenses.

3. *The Water of Condensation and the Condensed Water from the Evaporation of the Juice.*—The temperature of this water varies in the waste-pipe from 30-60° C.; it is contaminated by small quantities of volatile organic matter, ammonia, juice, also fats, fatty acids, etc. Since, as a rule, well-water, containing more or less lime, is used at the lowest possible temperature for condensing purposes, and the lime is partially separated owing to the heating by the vapours from the juice, this waste water is in this respect more pure than the original water. A portion of this large quantity of water is used for preparing the lime; it may also be used without hesitation for feeding the boilers, and, if necessary, for treating the bone-black, also, in very frosty weather, for washing the beet. The remainder, in case the quantity is considerable, must be cooled as much as possible by a suitable simple cooling-tower or terrace cooler, in which the heat should be regained, or by one of the surface coolers used in breweries; the water is then to be completely purified by the method of section 1 or 2, according to the locality. If the excess of water is not great, it will require no separate cooling.

Naprawil, in order to recover the fertilizing matters and to purify the waste waters, allows milk of lime to run in continuously.¹ The precipitate obtained settles in large flocks, whilst the water runs away quite clear. In 119 working days 3053 cwt. of lime, at a cost of 1005 fl. 95 kr. (£91 12s.), were used; the cost in wages was 190 fl. 89 kr. (£17 7s.); 26,228 cwt. of slime were obtained. The best method of removing and utilizing these waste waters is to employ them for irrigation.

The *separation or saturation mud* is the most abundant residue produced in sugar-works; several factories obtain in one season 15,000,000-20,000,000 kilos (15,000-20,000 tons).

¹ Kohlrausch, "Organ für Rübenzucker-Industrie"; Fischer, "Verwertung der Städtischen und Industrie-Abfallstoffe".

This residue frequently forms great heaps near the works, which, by reason of the decomposition which sets in, give rise to many inconveniences and complaints in the neighbourhood, and even damage the manufacture itself. This mud has only found one use on the large scale—as a fertilizer; yet it is rather harmful to calcareous soils, since it only contains 0·04 part of phosphoric acid and 0·35 part of nitrogen to 35 parts of lime. The author supposed that by carbonization a black substance could be obtained, which would find various uses.¹ The heating must be so conducted that the organic matter leaves behind carbon after its decomposition. This carbon has the advantage of being in a very fine state of division similar to a true chemical precipitate, so that the material, when squeezed between the fingers, feels like talc or soap. If it is attempted to carbonize the mass in large crucibles the portion in the middle is not sufficiently heated, whilst the portions at the sides are overheated; also at temperatures higher than a dark red heat the carbonate of lime is decomposed, the carbon being at the same time oxidized, so that only white lime remains.

It is therefore necessary to use another apparatus, the rotatory furnace of Casalonga being the best. This consists of a revolving cast-iron cylinder, which has a hollow axis, through which the tar and gas can escape. The cylinder makes only a few revolutions per minute. The dried mud is fed in at one end, and escapes at the other by a suitable arrangement after it has been carbonized. The substance obtained consists of an impalpable powder and of small harder particles, which are easily crushed. It is thoroughly powdered and may then be used as a black pigment. Its composition is as follows:—

¹ "Journ. des Fabr. de Sucre," 20, No. 36.

Calcium carbonate	78.500
Phosphoric acid	0.950
Ammonia	0.168
Ferric oxide and alumina	6.509
Silica	3.205
Carbon	7.500
Undetermined	3.168
	<hr/>
	<u>100.000</u>

The percentage of carbon varies according to the composition of the mud—in particular, according to the quantity of sugar it contains. The latter usually soon disappears owing to the fermentation which arises; it is therefore well to add to the mud before carbonization about 10 per cent of waste molasses. The shade of the black is more or less good according to the quantity of this addition.

The volatile products evolved during the carbonization deposit ammonia-water and tar in the condensers, whilst the gas is drawn off into the fires, where it burns with the production of much heat. The tar may also be burnt if a Deville furnace is used. The termination of the process is readily recognized by the blue flame which appears when the decomposition commences to yield carbon monoxide. The condensed water contains much ammonium carbonate, ammonia, and other nitrogenous compounds, including pyridine and picoline. In order to separate these products from one another the liquid is distilled with caustic soda solution, the distillate saturated with hydrochloric acid, and evaporated, when crystalline ammonium chloride is obtained. The mother liquor is precipitated by alcohol, which retains in solution the hydrochlorides of the organic bases, which are then set free by potash.

Further investigations of these products have been made by Etard;¹ they are similar to those obtained by Vincent from distillers' refuse. The principal product is naturally the black, which is suitable for use in size, oil-paints, and

¹ Zeits. d. Ver. f. Rübenzucker-Industrie," 16, p. 916.

printing inks. The cost is only 10 francs per 100 kilos (4s. per cwt.).

Skene, of Breslau, has given an account of the arrangements he employs for the waste matters.¹ The whole of the waste water goes on to 17.5 hectares (43.2 acres) of land, surrounded by banks; here the water cools; it is then drained off, and again filtered by passing through a meadow of 3.25 hectares (8 acres). The drainage is laid down in the ordinary system and is cut off by a valve, which is not opened until all the conduits have been pumped full. The irrigation works are so large that the water is only run off once in the season.

Purification of the Alumina which has been used for Clarification in the Manufacture of Sugar, in order to recover the Matter it contains.—The Brothers Lowig have patented four processes for this purpose.²

1. The used alumina is mixed with one equivalent of lime and ignited. Calcium aluminate is formed, the organic matter first leaves carbon or burns entirely on further heating. Ammonia, which can be recovered, is formed from the nitrogen in the organic matter.

2. The alumina is heated with magnesium chloride; magnesium aluminate is then formed, whilst the organic matter is destroyed by the hydrochloric acid produced, which can also be condensed and used later to dissolve the magnesium aluminate. The aluminates obtained in these processes (1 and 2) are converted into alumina by known methods.

3. The alumina is dissolved in the least possible quantity of hydrochloric acid, and the solution filtered from insoluble organic matter, e.g. albumin from plant juices containing sugar. Many of the organic substances which remain in solution can then be precipitated by the addition of alumina, or by the precipitation of a portion of the dissolved alumina, and then filtering off. The aluminium chloride may also be

¹ "Zeits. d. Ver. f. Rübenzucker-Industrie," 16, p. 916; Post's "Zeits. f. d. chem. Grossgew."

² *Ibid.*

ignited, and the organic compounds destroyed by the hydrochloric acid which is formed; but care must be taken that too violent heating does not result in the production of insoluble alumina.

4. The impure alumina may further be dissolved in caustic alkalies and thus freed, for example, from ferric oxide; then, if necessary, it may be purified by igniting the evaporated solution, and finally again be precipitated as the aluminate of an alkaline earth. The albuminous matters obtained in method 3 may be used as fertilizers or in the manufacture of ammonia.

See also "The Technology of Sugar," by J. G. McIntosh (Scott, Greenwood & Son).

CHAPTER XXVIII.

FRUIT.

Conversion of Fruit into Jelly.—Several recipes for this process are given in the following pages :—¹

Recipe of Siemens, of Hohenheim : Pears are crushed and pressed, the fresh sweet juice is boiled down to one-third of its volume in a clean copper pan, the scum removed, and the liquid cooled ; it is then strained through washed flannel. Whilst this is being done, about the same quantity of apples as of pears is well boiled with only a little water. The apples have previously been washed clean, but not pared or cut. When boiled soft they are rubbed through a hair-sieve of average mesh by means of a stiff brush, in order to separate the pulp from the skins and cores. The apple pulp is then mixed with the purified pear juice in the pan, and the two boiled together under constant stirring, until the mass adheres to a spoon in large lumps and, on cooling, has the consistency of a stiff paste. A slight addition of lemon peel, cinnamon, and cloves improves the flavour. In order to give the jelly a fine colour, about 0·5 litre of bilberry or elderberry juice is added to 100 kilos (1 lb.-200 lb.); a few green walnuts are also suitable.

All the jelly, whilst still hot, is brought into the vessels in which it is to be kept ; these, which should be previously warmed, are best of earthenware ; the jelly is not again disturbed before use. When the jars are full it is found advisable to bring them for some time into a very hot room, e.g. a baking oven, so that the jelly becomes covered with a very thick, hard crust. In order to protect the surface from the entry of

¹ Lucas, "Die Obstbenützung Deutsche allg. Zeits. f. Landw.," No. 26.

air, the jars are to be closed by a moist bladder. They are kept in a cool but dry place.

For fruit jelly all our sweet or less acid summer and autumn pears are suitable; of apples, baking apples, "rose apples," and other varieties ripening in the autumn. There need be no hesitation in using sourish-sweet or sweetish-sour apples, but a moderate addition of sugar is requisite. It seems to be established that the jelly from pure sweet apples and pear juice keeps longer than that in which sour apples are used.

Recipe for Lower Rhine fruit jelly: Equal parts of apples and common beet are separately half-boiled, then brought under a press together and the juice squeezed out. This juice is then placed on the fire and boiled down to a thick jelly. Pears may also be used without any different treatment being necessary: the juice is brought into a condition suitable for boiling, then freed from stalks, skins, cores, etc., and evaporated until it becomes a solid mass.

Sweet apples are generally used for such apple jelly; two of the best varieties are the *hürteling*, which is the most productive apple for jelly, producing 15-18 per cent of jelly, and the *keruling*. Neither freezes readily; they are kept through the winter on the ground in the open, later they are squeezed and boiled down to jelly. The fruit must be ripe for storing if it is to produce an abundance of fine jelly.

Manufacture of pure beet jelly, especially valuable in poor fruit-growing districts and in districts in which there has been a bad season. The apparatus next described and the manipulations may also be used for pure fruit jellies. After the beet has been freed from the cluster of leaves, it is washed in large tubs, or, better, in rotating lathwork drums; it then goes into a round copper pan, widening out above, in which it is boiled. In order to prevent burning upon the bottom, the pan is provided with a false bottom of strong wire cloth. During boiling the beet is continuously beaten and stirred to break it down. The size of the pan is arranged according to the quantity of beet to be worked. The quantity

of water is 8 litres to 100 kilos of beet (1 gal. to 125 lb.). The beet, boiled, and broken down, is then shovelled with iron spades into the press tub, which is provided with a grating or false bottom, so that the sap can readily flow away. This grating and the sides of the tub are lined with filter-cloth, which is also placed between the layers of beet pulp at intervals of about 6 ins. ; old coffee-bags can be employed in place of the filter-cloth. When all the contents of the pan have been introduced, they are covered over with filter-cloth, the wooden cover is put in position, and the vessel subjected to the action of (hydraulic) pressure. The expressed juice runs into a receiver, from which it is pumped back into the pan. The pan which was used for the first process is now used for boiling down the juice, or, on a larger scale, a second pan is employed, but in the former case the pan is very carefully cleaned by scouring with sharp sand. The evaporation then proceeds regularly ; towards the end a little oil or lard is added, in order to prevent frothing and burning on the bottom, the fire being also slackened. The consistency of the syrup is judged by the "thread" test : it is stiff enough when a thread 5 cm. (2 ins.) long can be drawn out between the index finger and thumb. A small spoonful of the syrup, placed in a shallow iron vessel and cooled in cold water, allows of the consistency being judged. One press is required for every two pans, one of which is used for boiling the beet, the other for thickening the juice. The whole process requires on the average a period of seven working hours. The finished jelly is, as a rule, first brought into earthenware pots, and then, when it has half-cooled, into the vessels in which it is to be kept.

The utilization of fallen fruit has been treated by a practical fruit-grower.¹ In the first place, it is not desirable to allow any fallen apples to spoil. The author collected the fallen apples in July, boiled them soft with much water, and then stirred up to a paste in order subsequently to obtain a jelly. The mass, which was obtained from quite green, un-

¹"Praktischer Rathgeber im Obst- und Gartenbau," 1898.

ripe apples, had a very unpromising appearance; however, the requisite sugar was added. The whole process therefore was as follows: The unripe apples were cleaned, brought into the boiling-pan, water added to cover them, and the contents then boiled and stirred until a fluid paste was produced. This paste was transferred to a coarse linen cloth and allowed to drain. The juice was then boiled with sugar to a jelly: 400 grms. of sugar to 1 litre of syrup (4 lb. to 1 gal.), the boiling being continued for about forty-five minutes. The jelly from unripe apples had a fine red-gold colour and a good flavour; its cost was quite low—i.e. rather less than 3d. per lb.

Preparing Dried Fruits.—A considerable amount of fruit such as apples, pears, plums, apricots, etc., is now dried or desiccated, in which condition it will keep indefinitely. Such fruit as apples and pears are first peeled, cored, and cut into thin slices, while from fruit containing large stones the latter are removed. The fruit thus prepared is then placed on wire gauze frames, preferably galvanized, or of aluminium, which are arranged one above another in a room through which a current of warm air is passed by means of a fan. In large installations the drying may be done in apparatus provided with moving endless bands or in vacuum drying machines.

See also "Recipes for the Preserving of Fruit, etc.," by H. Wagner; and "The Manufacture of Preserved Foods and Sweetmeats," by A. Hausner (Scott, Greenwood & Son).

CHAPTER XXIX.

WASTE PRODUCTS OF THE MANUFACTURE OF STARCH.¹

Utilization of the "Fruit Water".—In working by the ordinary process by which starch is obtained, the potato pulp coming from the grinding machine is diluted with so much water that the proportion of valuable constituents is reduced to such an extent that they cannot be utilized. This "fruit-water," if it has not fermented, may be suitably employed as a direct addition to pigs' food. If steam be available, it may be passed into the "fruit water" until the albuminous matters are coagulated into flocks, which are separated by running off the clear liquid into the drain, and using the residue as cattle food.

Utilization of the Pulp.—This mass is most suitably mixed with other cattle foods; since it is somewhat difficult of digestion, however, it is advisable to break it up by heating to boiling. The pulp still contains some starch which it may be profitable to recover. By suitable treatment 2-25 or even 3 per cent of the total quantity of starch may be recovered from the pulp, thus increasing the profits very materially. The pulp still contains many uninjured cells filled with starch which have escaped the grinding, and in order to break up these cells a simple arrangement is employed which drags the cells lengthway and thus ruptures them. The apparatus is constructed as follows: A roller of polished marble or granite is connected with a cog-wheel. Below this roller, but very near to it, lies a second one, also connected to a very much larger cog-wheel. Thus the upper roller makes three revolutions whilst the lower is making

¹ F. Rehwald, "Die Stärke Fabrikation," Vienna, Hartleben.

one. The pulp in passing between the rollers is at the same time squeezed and drawn out in consequence of the unequal speeds, by which means almost all the starch-containing cells are ruptured. When the rolled mass is brought into the cylindrical brush apparatus starch can be obtained from it in the same way as from the original material.

The process is generally conducted by collecting a quantity of the pulp, then rolling it and treating it alone. The starch which has been semi-dried and purified by settling also produces in this case a certain quantity of starch mud, which is treated either separately or together with similar material. In places where there is a distillery it is advisable to work up the residual pulp with the other material for the manufacture of spirit; by this means the whole of the starch is extracted, the cellular tissue going into the distillery wash.

If the pulp is collected into heaps, which are kept moist, a process of decomposition soon sets in which gradually but completely destroys the cellular tissue. The whole changes to a soft, cheesy mass, consisting of the decomposed cellular substance, starch and cellulose. If it be then brought into the apparatus for obtaining starch, the latter is obtained pure. For this purpose the pulp is allowed to lie in thin layers for a time, and, while still moist at the top, heaps are formed, 60-80 cm. high (24-32 ins.), resting on a layer of boards and covered by twigs or boards. After a few days the temperature of the whole heap rises (the covering of boards protecting it from cooling) and rapid fermentation sets in. In order to allow the air as much access as possible, it is advisable, in building the heaps, to insert poles and to draw these out carefully, so that channels may be formed into the interior of the mass. Repeated turning over with shovels and, if necessary, moistening with water, greatly accelerate the fermentation of the mass.

If the formation of gases of bad odour is remarked during this process, it is a sign that putrefactive fermentation is taking place in addition to the ordinary decomposition, by which the yield of starch would be diminished. A buttery or

cheesy smell denotes the occurrence of the butyric fermentation, by which the starch itself is attacked. This incorrect course of the reaction is due to the entrance into the mass of too little air, the mass being either too compact or too wet. This evil may be overcome by working the mass by shovelling, or by allowing it to dry somewhat.

Utilization of the Gluten.—In the process of fermentation just described the gluten is dissolved or destroyed with the exception of a small quantity, which rarely exceeds 25 per cent., but in the process without fermentation the yield of gluten may amount to more than 90 per cent of the total quantity present. In addition to the use of gluten as cattle fodder, for which purpose the gluten obtained by the process without fermentation is stirred with water and heated to 70° C., it is also used in the manufacture of foods. In the latter case the first operation is to obtain gluten-flour, as described by F. Rehwald (loc. cit.).

Wheat, from which the husk has been removed, is thoroughly washed; the starch layers obtained are not subjected to a further washing, but are partially dried by the air-pump and mixed with gluten. The mass is then rendered plastic by an admixture of potato-flour, or, in place of this, dark-coloured wheat-flour or pea or bean-flour may be used. It is of great importance to mix the gluten most intimately with the starchy substances, for which purpose a kneading machine, such as that used by bakers, is employed. The mixing may also be done by means of rollers, in which case a first pair of rollers produces a band of a certain thickness, which is stretched out more and more by the succeeding pairs of rollers. The thinnest band is collected, pressed together, and again subjected to the action of the rollers; by this means there is obtained by repetitions of the process a more and more uniform mixture of gluten and starch. It is advisable to add to the mass, before kneading, $\frac{1}{1000}$ of its weight of sodium phosphate and $\frac{2}{1000}$ to $\frac{4}{1000}$ of common salt. The paste is filled into a shallow rectangular box, with a narrow slit at one end, through which it is expelled by a piston. Below the

box is a long endless belt of linen cloth, running over rollers. When the paste is expelled through the slit in the box by means of the piston, it leaves in the form of a thin band, which is carried away by the endless cloth, from which it is taken on to boards. It is then dried in the sun to a thin, horny mass, which can be easily broken and ground to flour. This gluten-flour far surpasses beans in nutritive value; a food is obtained from it by stirring into boiling water, to which salt has been added.

The following process is used in order to obtain gluten in the form of groats. The gluten, made into a paste with potato-flour in the above-mentioned manner, is brought into a cylinder fitted with a piston, and closed at the bottom by a metal plate perforated by the largest possible number of holes. The holes are slightly conical, being about 1.5 mm. in diameter at the top and 1 mm. at the bottom. By applying pressure to the piston, the paste is made to issue in the form of thin threads, which are then cut up into small pieces by a knife below. The apparatus is arranged so that pressure is only applied intermittently, in order that the grains may be as far as possible of equal size. Below the cylinder there moves slowly a stretched endless cloth, which catches the grains and carries them away; they are then lightly dusted with flour. In order to round the grains, they are brought, together with 5 per cent of potato-flour, into a barrel, through the bottom of which passes an axle, and which is closed by a door in place of the bung-hole. The grains are rounded by the slow rotation of the barrel; finally they are sorted through sieves of different meshes, and dried in thin layers on boards.

Utilization of the Residues.—G. Thenius recommends a new method for the utilization of the residues obtained in the manufacture of starch,¹ which consists in evaporating the wash waters—the “softening” waters—which have previously been run to waste. By evaporating 10 grms. of this liquid, Thenius obtained 2.09 grms. of extract, which was

¹“Chem. Zeit.,” 150; Post’s “Zeits. f. d. chem. Grossgew.,” III, 2, 280.

of a pale brown colour, had a sweetish, salty taste, and an odour similar to that of malt extract. If the extract is dissolved in a little water, the less soluble salts—sulphates, phosphates, sodium and potassium chlorides—separate. The portion soluble in water is again evaporated to dryness on the water-bath; it then possesses a pleasant, sweetish taste, but is not salty. One hundred parts of the extract contained 25.6 parts of salts and 7.44 parts of pure extract. From a vessel of 15 hectolitres (330 gals.) capacity, 30 kilos (67.5 lb.) of extract are obtained. The extract can be profitably employed in bread-baking or in making cattle foods. The bread prepared with it is said to have an agreeable flavour, and to keep moist for a long time. The purified extract can be used medicinally, and as a substitute for malt extract. The extract is obtained by evaporating the liquor in shallow pans by means of the waste steam from the boiler.

Utilization of the Waste Waters.—In most cases the waste waters are run into a stream or sewer; they then frequently give rise to complaints, since the decomposable matter they contain ferments, and may thus taint the neighbourhood and injure the fish in the rivers.

As long ago as 1835, Burggraf made successful experiments on the use of this water for irrigating meadows and arable land,¹ and in 1877 Märcker gave an account of comprehensive experiments on the irrigation of meadows by its means.² The waste water, which is first run through two settling-tanks, in order that the fine grains of starch still suspended in it may be deposited, is conducted for a distance of 170 metres (185 yards) through a pipe 15 cm. (6 ins.) wide, with a fall of 33 mm. per metre (3.3 in 100). The water is received from the pipe in an open ditch 1 metre (39 ins.) wide and 30 metres (33 yards) long, which conveys it to a small storage pond. It is here mixed with pure well-water, in order to avoid the strong concentration of the original waste water, and to ob-

¹ "Polyt. Journ.," 56, p. 464.

² "Zeits. d. landw. Centralver. d. Provinz Sachsen"; "Dingler's Journ.," 25, p. 395.

tain larger volumes of waters for regular distribution over the meadows. The mixed waters are then carried to a large meadow of $7\frac{1}{2}$ hectares ($18\frac{1}{2}$ acres), over which it is distributed by a system of large and small ditches, and retained by dams. The water is conveyed away by a system of drains, which can be put in or out of action by sluices as required. The drainage then goes to a second meadow of 5 acres, and thence to a third of 6 acres. The crops obtained are described by Märcker as excellent.

Märcker observes, in conclusion, that the waste waters of starch-works may be applied to the irrigation of meadows with the greatest advantage, because there is not only an increase in the crop, but the composition of the hay is also considerably improved.

CHAPTER XXX.

BREWERS' WASTE.

Utilization of Malt "Combs".—These are an excellent food for cattle.

Utilization of Brewers' Grains.—They are used as food for cattle. For this purpose they should be employed as fresh as possible, since lactic acid readily forms, which then later produces butyric acid, acetic acid, etc. This objectionable alteration of the grains is recognized by the loss of the pure malt odour, the smell becoming distinctly sour. In feeding with grains it is necessary to add chopped hay or straw in order to cause the cattle to masticate. For a short period—about fourteen days—the grains may be kept in tanks, in which they are weighted down with boards and stones, and covered with water to a depth of several inches. The tanks must be kept very clean, and, when emptied, must be lime-washed until the coating does not turn grey—which is a sign that acid is present—but remains white. When required to be kept longer, brewers' grains are deposited in a pit in the ground and covered by a thick layer of earth. The pits should be of such a size that the grains in each are used in eight or, at the most, fourteen days. Fermenting grains are a valuable manure.

The following are analyses of two samples of dried grains from distilleries by A. H. Allen :—

	1.	2.
Moisture	10·32	8·00
Oil	6·70	5·07
* Proteids or albuminoids	19·88	19·80
Sugar, starch, and digestible carbohydrates	41·06	49·66
Woody fibre	19·00	13·16
Mineral matter	3·04	4·31
	100·00	100·00
* Containing nitrogen	3·14	3·13

There are four methods of preserving grains to be considered. The first, drying in the kiln, gives very good results, but the process is too expensive. The second, which is coming into use in England, consists in expelling the moisture in centrifugals, into which live steam is conducted; the grains then become pressed into solid cakes, which are recommended as a most excellent food for cattle. In another method, the grains, mixed with other suitable foods, such as bran, meal, peas, beans, etc., are mixed up to a paste, and baked into a kind of bread. The product is brown, porous and friable, smells and tastes similarly to fresh rye bread, mixes with water, and may be given dry mixed with other chopped fodder, and also as a drink. Finally storage, with an addition of common salt in pits with cemented brick walls, is said to have been effective.

Utilization of the Yeast.—Pressed yeast, commonly known in England as German yeast, is produced from distillers' yeast, but not from brewers' yeast, which is difficult to purify and does not keep so well. H. Rüdinger gives the following account of its preparation:—¹

After the termination of the main fermentation, the yeast which has separated in the fermenting vats is collected in a large tub, provided with a series of plugged holes in the side. The mass is left at rest for some hours, when the yeast settles, and, by opening the upper holes, a quantity of raw beer may be obtained, which is either put into a barrel or added to the fermenting vat in the next fermentation. After this beer has run off the tub is filled up with clean water, the whole well stirred and allowed to deposit. After about an hour the liquid again begins to run off. The upper holes are opened; the liquid, which is at first clear, is removed, but when it begins to be somewhat turbid it is run through a sieve, on which a wet coarse linen cloth is spread. The linen retains the greater portion of the yeast; but after some time the pores of the cloth are so filled by it, that the liquid

¹ "Die Bierbrauerei und Malzextract-Fabrikation," H. Rüdinger, published by A. Hartleben, Vienna, 1887.

runs away very slowly. It is therefore necessary to have several sieves in readiness so that the operation may not be stopped.

The removal of the liquid, by opening the lower holes, is continued until the yeast begins to appear as a thick liquid, when the holes are again closed. The yeast on the linen is removed and returned to the tub, which is again filled with water, and the yeast treated exactly as before. This washing is continued so long as the yeast on the linen has a perceptibly bitter taste. In most cases three or four treatments of the yeast, with fresh quantities of water, are sufficient to remove the bitter taste to the required extent.

The washed yeast is now collected and freed from water, for which purpose a system of filters is arranged near the yeast-tub. The uppermost part of this apparatus is a fine hair-sieve; below this are placed several frames, across which linen cloth is stretched, being hung at the four corners of the frame to wooden pegs by means of stitched-on loops. The turbid liquid coming from the uppermost cloth leaves a portion of its yeast on the next, also on the third, and so on, finally leaving the last cloth with only a slight turbidity; it is received in a tub, where it deposits the remainder of the yeast as a fine, slimy residue, whilst the supernatant liquid is quite clear.

The pores of the filter cloths soon become filled to such an extent by the fine particles of the yeast that only a little liquid can pass through; frames in this condition are removed, allowed to drain spontaneously, and replaced by fresh frames. When finally all the liquid has been brought from the tub on to the filter frames, the latter are allowed to stand until no more liquid drips from them. The yeast now appears upon the cloths as a brownish-coloured soft mud, which is removed by spreading the cloths out flat, and scraping off the yeast with a blunt wooden blade.

The paste is now brought into a very strong cloth (press cloth), this is surrounded by a second cloth, and the whole brought under a screw press, where at first a gentle pressure

—the liquid should not run away turbid—and then gradually a considerable pressure is applied. When once a considerable quantity of water has been pressed out of the yeast, the pressure may be allowed to rise tolerably high, so that the compressed yeast taken out of the press cloths is a mass which may be compared in consistency with new cheese.

In order to be able to keep the pressed yeast without alteration, it is found advisable at once to divide it into rectangular blocks of definite weight (500, 250 grms., i.e. about 18 or 9 oz.), which are then wrapped in oiled paper, tinfoil, or canvas, and kept in a cool place.

Utilization of the Bottom Yeast.—If bottom yeast is to be converted into useful bakers' yeast, it requires to be washed. It is first run through a fine hair-sieve into a vat, which is somewhat deeper in front than behind. In the front wall of this vessel, in the middle stave, which is somewhat thicker than the others, in order not to lose strength, are bored holes at intervals of 5 cm. (2 ins.) at the top, and at smaller intervals below; the holes are now closed with plugs. The yeast is stirred with water, to which a teaspoonful of powdered ammonium carbonate is added per hectolitre of yeast (22 gals.). When the yeast has settled the plugs are drawn one after the other, and the water allowed to run off. The yeast after this treatment is rarely sufficiently pure, so that the process must be repeated a second and third time. The second time less ammonium carbonate is added; the third time, none.

This process is occasionally also used for top fermentation yeast, in which case two additions of water, without the salt, are generally sufficient. When the yeast is white enough, it is filled into press bags and well pressed; it is also frequently kneaded with starch, partly to improve the colour, partly to give it more the nature of a so-called short or crumbly yeast, but this is now regarded as an adulteration; such yeast keeps better but it is naturally weaker in its action.

Some little time ago a yeast extract was prepared by boil-

ing yeast with water, straining and evaporating the liquid. This was remarkably like extract of beef in odour and taste, and was used for adulterating the latter; its detection and exposure, however, soon put an end to this form of sophistication. It is, however, particularly rich in nitrogenous matter, and therefore there is no reason why it should not be used in a legitimate manner as a food product.

Dried Yeast as Food for Farm Stock.—According to C. Crowther,¹ dried brewers' yeast is used on a large scale in Germany for feeding cattle, and in England there are several places at which yeast is dried, principally for export, the amount being from 2000-3000 tons annually. The average composition of the material is:—

Moisture	4.3 per cent.
Proteins	48.5 " "
Oil	0.5 " "
Fibre	0.5 " "
Ash	10.7 " "
Soluble carbohydrates	35.5 " "
	<hr/>
	100.0

Feeding experiments have been carried on with this material in Yorkshire, which show that it is quite safe to use for cows, calves, and pigs, but cows do not seem to take to it owing probably to its bitter flavour. Owing to its high content of proteins it should be mixed with other feeding-stuffs such as grain or oil-cake.

Utilization of the After-worts.—These are advantageously employed, instead of water, for mashing the malt of the next mash, if that takes place immediately after the one from which the after-worts were obtained. If it would be necessary to wait only several hours, it is advisable to use the after-worts together with the wash-water of the grain for preparing malt vinegar. For the same purpose, i.e. vinegar, all other residual liquors—the last portions of the beer, which are turbid owing to the presence of yeast, etc.—may be employed.

¹ J. Board Agric., 1915, 22, 1-10.

For the last-mentioned purpose a wide but low vat, provided with a cover, is brought near the brewing vessel, the liquids enumerated above being brought into this vat. In order to commence the formation of vinegar, a few glasses of sour beer or some "mother of vinegar" are added. After the liquid has stood for some hours in this vat, it is drawn off into smaller vessels, placed in an airy situation at an ordinary room temperature. If the vinegar is found to be too weak, one-hundredth of its volume of distilled spirit may be added, for which purpose the crude distillate is quite suitable.

Utilization of the Deposit in the Coolers.—This deposit may be used as fodder in conjunction with brewers' grains or distillery wash.

The Utilization of Spent Hops as Cattle Food has been treated upon by O. Kellner.¹

The spent hops (according to Kellner), on account of their composition, which corresponds to that of red clover hay of medium quality, have recently been much recommended for fodder. Since, on the one hand, this refuse is produced in large quantity and has hitherto been utilized to an inadequate extent, and, on the other hand, it was of great interest to learn the behaviour of such an extracted vegetable substance towards the digestive juices, Kellner undertook to ascertain the digestibility of spent hops by a direct nutritive experiment. The results showed that the digestive coefficients of the constituents of hops, with the exception of that of the crude fat, are lower than have hitherto been found for any food directly tested for digestibility. Since the extraction in the brewing did not afford a sufficient explanation of this remarkable result, other conditions were included in the scope of the observations. It was then found that about 24 per cent of the crude fibre is lignin, which, being in intimate admixture with the cellulose, considerably decreases the digestibility of the latter. Also in spent hops a portion of the protein is found in combination with tannic acid, which

¹ "Deutsche Landwirtschaftliche Presse," 1879, No. 55, pp. 332, 333; Biedermann's "Centralbl. für Agriculturchemie," 1879, No. 9.

is known to hinder the action of the digestive juices. Only the crude fat had a normal digestive value. Since this constituent of hops is certainly composed of substances which have not the chemical constitution of ordinary fats, it may also be assumed that the digestibility of the hop fat is not equal to that of the ordinary fats.

Thus, in consequence of the low digestibility and the reluctance with which cattle eat spent hops, this substance cannot find any extensive use as fodder.

The residues in question are best employed in preparing compost, perhaps after the residual portions of the wort have been removed by water, to be further utilized in beer. Small additions of hops to the daily food are not to be rejected, since the appetite of the animal is increased thereby. The proposal of Pott, to add spent hops in place of the usual straw to the cakes of distillery and brewers' grains, appears to be worthy of attention, especially since the tannin in the hops has probably a preservative action. For the same reason spent hops might perhaps be used with advantage in storing sliced beet, etc.

The best method for treating *malt "combs"* for use as food or manure consists in grinding to a coarse meal, after well cleaning and removing dust. This substance must always be mixed with other foods; it is most suitable for improving a ration of chopped straw. After grinding, the "combs" are more easily acted upon, and hence are more digestible. The same reason holds good when malt "combs" are to be used as a fertilizer. From experiments of A. Fericka it appears that the differences in the vegetation obtained with different manures are very considerable, and that ground malt "combs" treated with sulphuric acid afford the best means of increasing the growth of grass. The process of treating the ground "combs" with sulphuric acid is as follows: In a large tub, 5 cwt. of the ground "combs" are steamed, with a gradual addition of boiling water, until a paste is produced, which is left at rest for two hours, after which the whole mass swells up considerably; it is then found

that the meal has absorbed the whole of the water, no more remaining at the bottom of the tub. Then the mass is again scalded, this time with an addition of about 10 lb. of sulphuric acid to the boiling water. After cooling, the material can be at once used for manure; it is especially suitable for incorporation in poor composts.

Waste Waters of Distilleries.—The spent wash or “pot ale” left in the stills after evaporation of the spirit contains a considerable amount of organic matter with a comparatively high percentage of nitrogen. Wherever possible this is run into the sewers or streams, but such a proceeding is not desirable. It is somewhat difficult to purify, and some little time ago a valuable prize was offered by the Scotch distillers for a method of utilizing it. It could be purified by the septic process or evaporated, and the residue mixed with the spent grains for cattle feeding, but would scarcely repay the cost of fuel.

Separation of the Fusel Oil.—In the fermentation of sugar and saccharine matters, especially that which is obtained from potatoes, a certain proportion of higher alcohols—particularly amyl alcohol—are formed. These are separated from the ethyl alcohol and water by rectification or fractional distillation, and form fusel oil. This is redistilled, the portion passing over at about 131° C. being crude amyl alcohol. Amyl alcohol is used to a certain extent in the manufacture of varnish stains and also for the production of amyl acetate or pear essence, which is now used very largely as a solvent for nitrocellulose in the manufacture of celluloid varnishes.

See also “Industrial Alcohol,” by J. G. McIntosh (Scott, Greenwood & Son).

CHAPTER XXXI.

WINE RESIDUES.

Utilization of the Marc.—This is the residue from the wine-presses, consisting of the skins and seeds of the grapes together with more or less stalk. The utilization of this material extends to the production of tartaric acid, the preparation of marc brandy and cœnanthyllic ethers, the production of illuminating gas, Frankfort black, and grape-seed oil. To these are to be added the methods used by wine-growers for utilizing the marc: the production of marc brandy and after-wine, the preparation of wine vinegar from the marc, the use of the marc in making verdigris, the consumption of the marc by cattle, its use as fuel, and the recovery of potash from the ash.

Utilization of the Crude Tartar.—To this division belong the preparation of tartaric acid from crude tartar and calcium tartrate, the preparation of cream of tartar and the more important tartaric acid compounds.

Utilization of the Lees.—The principal products are: lees brandy and cœnanthyllic ether, calcium tartrate and cream of tartar, Frankfort black, and lees wine.

We must here abstain from dealing further with this highly important industry of waste products, which is so extremely profitable in wine-growing districts, since a special work on the subject has just been published, which is highly to be recommended. In it the utilization of all the wine residues is described in so thorough a manner, easy to understand and highly practical, that the whole work would have to be reproduced if we were to deal with the subject. We therefore refer anyone who intends to undertake the treatment of wine residues, which is extremely profitable in

wine-producing districts, for instruction in the necessary arrangements and method to the book "Verwerthung der Weinrückstände," etc., by Antonio dal Piaz, Vienna, Hartleben. To this practical work we add here, in regard to the treatment of wine lees, only the process by which the firm of Wagemann, Seybel & Co., of Giesing, near Vienna, produces tartar and tartaric acid from the substance.

According to E. Kopp,¹ 4000 cwt. of tartaric acid are produced by this firm. The wine lees, which deposit separately in the spring after the main fermentation, amount to about 5 per cent of the wine. They were at one time used only as manure. Since 1854 Seybel has successfully endeavoured to facilitate the utilization. The process begins by subjecting the lees to high pressure in filter presses, 100 eimer (58 hectolitres or 1276 gals.) then produce 40 hectolitres (880 gals.) of wine and 20 cwt. of dry lees. With the yearly production of about 4,000,000 eimer of wine in Austria, the lees deposited amount to 60,000 cwt., and represent a value of over 4,000,000 francs (£160,000). The pressed lees contain organic matter, yeast cells, etc., tartar, tartrate of lime, colouring matter, clay, and sand; they are treated with hot dilute hydrochloric acid, which dissolves principally the tartar and tartrate of lime. The liquid, after filtering through woollen cloth, gives, on cooling, crystals of tartar, which can be purified by recrystallization. The mother liquors, when neutralized by milk of lime, give a precipitate of tartrate of lime, which is converted into tartaric acid. From the last impure mother liquors of the tartaric acid a further quantity of tartar is obtained by the addition of potassium chloride.

A process introduced by Müller and Schlosser, of Vienna, for the recovery of tartaric acid from the deposits in discharging vats, is allied to the above treatment of wine lees. It is well known that tartaric acid is used in considerable quantity for discharging printed Turkey-red fabrics; it is then precipitated in a bleaching powder vat as tartrate of lime. The method of treatment is not known, but is readily

¹ "Naturf. Ges. in Zurich"; "Neueste Erfindungen und Erfahrungen".

imagined. It would be very convenient to combine it with the treatment of wine lees. The calcium tartrate from the discharging vats contains excess of lime, which could serve for neutralizing the hydrochloric acid decoction of the lees.

Among the applications of grape marc Pasque gives attention to the production of oil,¹ which, according to Pezeyre, is very simple and profitable. The well-dried marc is stirred to a paste, brought into a pan, frequently well stirred, boiling water added—1 gal. to 4 gals. of marc—and, as soon as the oil exudes, the whole mass is brought to the press. The oil obtained is pale yellow and odourless; it can be used for burning purposes, and, when sufficiently purified, for culinary use, but it should not be long kept, since it soon becomes brown and rancid. The oil-cakes may find application as fuel in distilleries; the ash forms an excellent manure for vineyards, being very rich in potash.

The firm of D. Savalle fils et Cie., of Paris, has constructed a special portable apparatus for the production of alcohol from grape marc.² Although this apparatus cannot be taken to every vineyard on an ordinary wagon, yet it can be taken to some one vineyard, to which the marc from the neighbouring vineyards can be inexpensively and simply removed. Not only is the pressed grape marc to be distilled, but also the fluid residues obtained after the fermentation and repose of the wine, the deposit and the lees. With such a method the co-operative spirit is a necessity, for several, or many, vine-growers would have to combine to obtain the apparatus; they would then treat their residues in turn according to agreement.

¹ "Giorn. agr. Ital."

² "Oesterreich-ungarische Brennerei-Zeitung."

CHAPTER XXXII.

INDIA-RUBBER AND CAOUTCHOUC WASTE.

Utilization of the Waste.—According to Grote, in Muspratt's "Chemie," Goodyear grinds the waste from vulcanized caoutchouc in a rag engine, mixes with it pure caoutchouc similarly divided, passes the mixture between heated rollers in order to obtain thorough incorporation, then adds a quantity of sulphur corresponding to the pure caoutchouc, and afterwards proceeds as in the manufacture of vulcanized caoutchouc.

Bacon disintegrates the waste of vulcanized or hardened caoutchouc or gutta-percha, then pours 10 kilos of carbon bisulphide and 250 grms. of spirits of wine over 100 kilos of the waste, and allows the whole to stand for two hours in closed vessels, when the mass is found to be so soft that it can be ground and used again in the manufacture of new objects. The degree of softening can be regulated by the quantity of the carbon bisulphide mixture and the duration of the action.

Parkes (according to Grote in Muspratt's "Chemie") boils 8-10 kilos of the disintegrated waste in a strong solution of 20 kilos of calcium chloride until the gutta-percha or caoutchouc has become soft, and two pieces can be readily united by kneading. The lumps taken out of the liquid are washed first in a hot alkaline liquor, then in hot water, after which, according to the statements of the patentee, they can again be worked up.

Newton desulphurizes caoutchouc waste by softening it in camphine (distilled turpentine) for two to fourteen days, according to the extent of the vulcanization. If much sulphur was used in vulcanizing, or if lead compounds are present, it

offers considerable resistance to the camphine. The treatment is in every case continued until the waste is well softened throughout, when it is heated in a still at 65-71° C., adding camphine from time to time, so that the waste is always covered with liquid. It is convenient to add in this operation 15-25 kilos of ether and 5 per cent of spirits of wine, and then continue the heating until the waste has regained its natural condition, for which one to two hours are requisite; the whole is then dried at a gentle heat. The addition of spirits of wine prevents the residues from remaining sticky, but may be omitted if this is immaterial. The use of a still effects the recovery of the evaporated solvent.

Later, Dodge recommended to disintegrate the waste as completely as possible and then expose it to a temperature of 150° C. in a cylinder surrounded by another cylinder, steam being supplied to the space between, until it had become quite plastic, when it was mixed with fresh rubber mass, or to 25 kilos of waste, 100 grms. of palm oil, 170 grms. of sulphur, and 1.5 kilo of white lead, zinc white, magnesia or clay may be added, and the whole well kneaded.

A new and improved process for utilizing the caoutchouc contained in the waste of caoutchouc goods, and for recovering the zinc present in them, is due to Burghardt, of Manchester, and has been patented in England. In this process the waste is thrown into a vessel of wood or lead, and covered with the requisite quantity of hydrochloric acid of a strength sufficient to destroy adherent cloth and fibres completely; the mixture is then boiled until the caoutchouc is freed from all fibres. The solution contains zinc and calcium chlorides, and occasionally also lead chloride; it is treated as described below. The vulcanized rubber is now brought into a vessel containing water, which is boiled until all the acid and zinc, calcium, or other chlorides are removed from the rubber. The caoutchouc thus purified is now dried, and mixed with sufficient spirit, coal-tar naphtha, wood-naphtha, petroleum, turpentine, carbon bisulphide, benzene, or other solvent for rubber, in a jacketed vessel of wood, copper, iron, or lead, the vessel closed, and the whole brought to a temperature of about 115°

C. by means of steam, gas, or hot air, until the caoutchouc is dissolved or converted into a thick pasty mass. When this is the case, the naphtha is distilled off at a temperature not exceeding 100° C. The above-mentioned solution is treated in a vessel with sodium bicarbonate, soda crystals, anhydrous sodium carbonate, ammonium carbonate, potassium carbonate, the carbonates of the alkaline earths, caustic soda, caustic lime or its solution, or caustic potash, in quantity sufficient to precipitate the zinc, calcium, or lead from their solutions. The precipitate is ground in a current of water, by which the calcium carbonate, which is specifically lighter than the zinc carbonate, is carried away. The zinc carbonate is either dried and sold as such, or dissolved in hydrochloric acid, sulphuric acid, or other acid, and sold as zinc chloride, sulphate, or other salt. Or the solution can also be concentrated to a suitable extent and used as a mordant for cotton.

Ludwig Heyer, a rubber manufacturer of Berlin, applies the following method *to the recovery of old vulcanized caoutchouc*: Old discarded buffer rings of railway wagons are heated in the presence of steam. The sulphur distils off, the caoutchouc melts and flows into hot water, where it collects at the bottom of the vessel. The steam prevents the material from burning. The melted caoutchouc has acquired essentially different properties; it has become a tolerably fluid dark mass, which also remains liquid at the ordinary temperature, soon dries in the air, and has retained the property of being waterproof. On the other hand, it has lost the elasticity, at least in thick pieces. Heyer employs this fluid caoutchouc principally for preparing waterproof sheets for wagons, railway trucks, ships, etc. It may also be recommended as a waterproof varnish for ironwork.¹

Dankwerth and Köhler, of Petersburg, have patented a *process for the treatment of old or perished caoutchouc, in order to obtain from it oils, varnish, and materials for mixing with caoutchouc and other substances*. Old or perished caoutchouc is subjected to dry distillation in a retort by means

¹ "Chemiker-Zeitung," 1880.

of fire and superheated steam. Volatile constituents of the caoutchouc pass over, which, when condensed, form oils and a substance which has, after vulcanization, to a great extent the properties of natural caoutchouc. The lighter oils, distilling at 60-105° C., are separated from the heavier oils. The former serve directly for the preparation of varnish, the latter are mixed with hempseed, linseed, or other vegetable oils, and then converted into boiled oils by boiling or chemical action. The mass still to be subjected to vulcanization is intimately mixed by means of rollers, and then 7-20 per cent of sulphur added.

A very durable *varnish from old rubber waste* can be prepared for various purposes¹ by heating 2 kilos of old rubber, 4 kilos of colophony, 4 kilos of boiled linseed oil, and 0.5 kilo of sulphur in an iron pan until all are equally dissolved. When this is the case, whilst the liquid is still hot, 4 kilos of rectified American spirits of turpentine are added, and then the liquid is diluted with about 10-12 kilos of boiled linseed oil. The varnish may be coloured with earth pigments as desired, or left in its original state. When uncoloured the varnish has a honey-yellow colour, similar to a dark copal varnish. It is particularly recommended for varnishing the lead roofs of bleaching-powder chambers; its resistance to free chlorine has been tested for years. The varnish is very brilliant; when good boiled oil is used in its preparation it dries within several days.

One of the latest processes for the recovery of india-rubber is that in which terpineol is employed. India-rubber, both vulcanized and unvulcanized, is soluble in terpineol, which also dissolves the resins, etc. By addition of alcohol to this solution fairly pure india-rubber is precipitated, while the alcohol and terpineol can be recovered from the residue. This is probably the only process in existence for successfully treating waste rubber.

As a rule waste rubber is utilized by grinding it up and adding it to fresh rubber with the other ingredients. It can-

¹Campe, "Oel- und Fettindustrie," 1890; "Neueste Erfindungen und Erfahrungen".

not be regarded as improving the material, but it simply serves the purpose of a "filler".

Artificial caoutchouc is made in the following manner: In an iron pan about 10 lb. of sulphur or flowers of sulphur are heated with 20 lb. of rape oil, with constant stirring, until the sulphur is melted and a point is reached at which the mass swells up. At this instant the mass must be rapidly poured out, either into a mould dusted with any kind of flour, or on to stone plates wetted with water. The mass solidifies and has similar properties to caoutchouc; it is soluble in linseed oil. The mass may also be prepared from linseed oil, but less sulphur must then be taken. The pan should only be half filled, otherwise the mass would boil over.

The rubber substitutes or surrogates are, however, usually prepared by mixing linseed or rapeseed oil with sulphur chloride, which immediately combines with them to form solid gelatinous elastic substances, which are largely used for mixing with india-rubber in order to cheapen that product.

White substitute is prepared by treating the oils in the cold, and brown substitute under the influence of heat, the proportions being about 100 parts of oil to 25 parts of sulphur chloride.

Extraction of Resins from Crude India-rubber.—India-rubber always contains a proportion of oxidized substances which owing to their properties are known as resins. They do not resemble ordinary resin as their acid and saponification values are very low, but they have some properties in common. The amount of resin in rubber varies from 3 per cent in Para to 50 or more per cent in the crude African rubbers. For the purpose of purifying the latter and thus increasing their value the resins are extracted in some form of closed extraction apparatus by means of acetone. The acetone is distilled off in a current of steam and the melted resin run into barrels. At present there is not much demand for this product, but as it becomes better known no doubt a variety of uses will be found for it.

See also "India-rubber and Gutta-percha," by T. Seeligmann, etc. (Scott, Greenwood & Son).

CHAPTER XXXIII.

AMBER WASTE.

Utilization of the Waste.—Attempts have been made to weld amber cuttings together by heat, but never with great success, the mass obtained having lost somewhat in beauty of colour by being browned by the heat. A better process is the following: After the cuttings have been sorted according to size, they are treated for several hours by solvents such as carbon bisulphide, ether, etc. A plastic mass is obtained, which is spread out on a table so that the excess of solvent may evaporate, when it is compressed under great pressure into the requisite moulds.

In certain cases it is found advisable in this process to apply a gentle heat in order to unite the isolated parts, and to press them better into the moulds.

The pieces obtained, which have already the general shape of their final form, are further worked in the ordinary manner and then polished.

Whilst the lumps of amber welded together by the old process are very brittle, those obtained by the process just described are characterized by great elasticity. Holes may be bored in them without fear of cracks or chips, which often occur in the pieces amalgamated by heat alone.

In order to obtain articles of a cloudy or speckled appearance, small pieces of hard amber are mixed with the plastic mass; these pieces, when they differ in colour from the general mass, give the article a novel appearance.

The waste amber turnings, etc., and the dark and small pieces are sold to varnish manufacturers for the manufacture of amber varnish, probably the most durable varnish known.

Legend has it that the old violins were varnished with amber varnish which is regarded as imparting the purity of tone for which some of these instruments are famous; it is also supposed that the method of making this amber varnish is a lost secret.

On distillation of amber an oil is obtained known as "oil of amber" together with succinic acid which has some claims to be regarded as a preservative.

See also "The Manufacture of Varnishes," Vols. II and III., by J. G. McIntosh (Scott, Greenwood & Son).

CHAPTER XXXIV.

UTILIZATION OF TURF OR PEAT.

TURF or peat occurs in very large quantity in various localities in boggy places. It is the product of the slow decay of vegetable matter under water, and in some respects resembles coal. Peat is a dark brown solid varying in appearance from a loose friable earthy product to a hard tough mass very nearly approaching coal, the former being found on the surface, the latter at depths of several feet. In Ireland, in Yorkshire, and parts of Scotland, etc., the peat is regularly cut every year into the form of blocks which are air dried and used as household fuel.

Peat varies very considerably in composition, but it invariably contains a large percentage of water and mineral matter and hence has not a very high calorific value. The following is an analysis of a sample peat dried at 100° C. (Johnstone):—

Carbon	59.00
Hydrogen	5.50
Oxygen	19.50
Nitrogen	1.50
Mineral matter	14.50
	<hr/>
	100.00
	<hr/>

In the wet state peat will contain 60-65 per cent of water and in the air-dried state 25 per cent, so that difficulty is found in drying, whilst on burning the evaporation of this water requires a considerable amount of heat, hence as compared with coal, peat is a poor fuel.

Many attempts have been made to utilize peat, and in this connection a very able paper by Dr. Dvorkovitz on the "Distillation of Peat"¹ may be consulted.

¹ "Journal of the Soc. of Chem. Indt.," 1894, p. 596.

The lighter and more flocculent peat is baled and sold as "peat moss litter," used as bedding for horses and cattle, for which purpose it is very well suited.

Peat moss is also ground up and saturated with common beet molasses, passing under proprietary names as a cattle food.

By suitable treatment peat can be spun into yarn, while a proportion of it is available as a low-class papermaking material.

Peat is also compressed into briquettes and used as fuel. The distillation of peat is also carried out in the same way as coal yielding illuminating gas and other products. Both these processes will be considered in subsequent chapters.

Utilization of Turf Waste.—G. Gercke, jun., of Hamburg, has patented a process for producing plastic objects from turf as a substitute for wood, pasteboard, paper, etc. This process is based upon obtaining the turf without damage to the fibres, which are easily injured whilst moist. In removing the turf, in order not to cut through the fibres, the longitudinal layers must be followed, which occasionally form flat sheets.

After the raw material has been cut to the desired dimensions, it is dried upon boards or a framework of laths, during which it is protected from the sun in order to prevent the plates from warping. When completely dry, the material is subjected to a special treatment, the essential part of which is strong compression, according to the particular purpose for which it is required. The very hygroscopic constituents of the product must be removed if it is to be exposed to the action of the weather. For example, in order to make a roofing material, the dry turf plates, compressed to 10-20 per cent of their original thickness, are protected from moisture by saturation with a heated mixture of tar and asphalt. The excess of tar is removed by squeezing between rollers and the plates then dusted with sand in order to prevent them from sticking together.

Another method consists in saturating the turf plates with

milk of lime, drying, pressing or rolling, soaking in water-glass and then coating with water-glass paint.

In order to increase the strength of the plates, which is already considerable, materials of various kinds are inserted and fastened between two or more of the layers by means of a suitable adhesive agent. For this purpose bast, tow, cord, long turf fibres, heather, twigs, metal or waste wood are suitable, the binding and impregnating materials being tar, asphalt, wood cement, glue, water-glass, varnish, pitch, clay and resin cement.

The compressed turf may be subjected to any required treatment; it is suitable for replacing papier-maché and wood-pulp, wood, horn, bones, etc.¹

Obtaining Oils, Spirits, and Gases from Peat, etc.—No. 11481 of 1915.—A. N. Hacnicol, 31 Queen St., Melbourne, Australia, claims: (1) A process for the extraction of oils, spirits, and gases from peat or other materials or substances consisting in first grinding the material and continuously or intermittently feeding the substance by pressure or otherwise into a retort, and applying a heat gradually and regularly externally of the retort, subjecting the material in the retort to the action of steam which may be superheated, the substance being passed over the heated surface by a moving rabble, the retort being partitioned to provide heat sections, and the volatilized substances emanating from the material treated being led off by pipe connections to a condenser or condensers, the oils and spirits being collected in a reservoir or reservoirs by condensation, the non-condensable gases being returned to the furnace to be used as fuel, and the hot gases flowing from one part of the apparatus to another part being utilized for drying the substances before they are fed into the retort. (2) Apparatus for the extraction of oils, spirits, and gases from peat or other materials or substances by the process set out in claim 1, having in combination a retort chamber, rabbles within the retort chamber, and arranged to pass over the surface of the retort, means for dividing

¹ Compare T. Koller, "Die Torf-Industrie," Vienna, Hartleben, pp. 109 et seq.

the retort into neat sections, a feeding hopper at one end of the retort, a feeding conveyor adjacent to the hopper, means at the opposite end of the retort adapted to expel the material after being treated, means dividing the retort chamber below the floor into a plurality of flue compartments, a source of heat adapted to heat said compartments, means for driving the rabbles over the floor of the retort and pipe connections, and a fan or blower between the retort and condensers.

(3) An apparatus for the extraction of oils, spirits, and gases as claimed in claim 2, wherein the retort chamber is constructed of refractory material, partitions divide the retort into heat sections, and the plurality of flue compartments receive heat independent of each other and extend longitudinally to the floor of the retort within the chamber of refractory material. (4) An apparatus for the extraction of oils, spirits, and gases as claimed in claim 2, wherein the rabbles passing through said heat sections progressively carry material to be treated over one end of the retort to the other, and the source of heat is connected with said flues adjacent to the delivery end of the retort, means being provided for withdrawing the gases independently from the several heat sections, and for conducting the non-condensable gases to the said source of heat where they are used as fuel.

(5) An apparatus for the extraction of oils, spirits, and gases as claimed in claim 2, wherein the rabbles extending transversely across the retort carry rollers at their end separated from the heat sections of the retort. (6) An apparatus for the extraction of oils, spirits, and gases as claimed in claim 2, wherein the rabbles are adapted to pass over a relatively cool surface between the platform and the roof of the retort and above the heat sections. (7) An apparatus for the extraction of oils, spirits, and gases as claimed in claims 2 and 3, wherein the partitions forming heat sections are carried down to the surface of the material under treatment. (8) An apparatus for the extraction of oils, spirits, and gases as claimed in claim 5, wherein the rollers of the rabbles are adapted to operate in a cooler zone formed by an extension of the retort and a partition.

CHAPTER XXXV.

MANUFACTURED FUELS.

Artificial Fuel.—In the year 1874, Ney, at a meeting of the Aix-la-Chapelle Society of Engineers, confirmed the statement which originated in Belgium, that a mixture of 80 lb. of soil with 20 lb. of small coal, moistened with a solution in water of 1 lb. of soda or common salt, burnt well. This amount of coal, which by itself would only last fifteen minutes, in combination with the other materials burnt for an hour. This is, however, merely a retardation of burning, there is no gain in the actual heating value. It is explained by the fusion of the soda and the earthy constituents of the soil, to form a slag below which, owing to the impeded circulation of the air, the fire burnt for a long time. Naturally, direct action of the soda on the fuel is not to be imagined. R. Hasenclever, on this occasion, called attention to the high proportion of combustible matters in certain soils. Thus street mud from Stolberg, near Aix, according to his researches, contained not less than 20-21 per cent of combustible material; whilst dirt from the Römerstrasse, in Aix, only contained 6 per cent. The choice of the soil is therefore of importance. At Hasselt, in Belgium, where the discovery of the above artificial fuel was made, there are many cavities filled with turf-like soil. When such soils are not at hand, the process is devoid of importance. The mixture, as might be anticipated, has been found quite suitable for firing boilers.

Manufactured Fuel.—Loiseau¹ prepares a fuel, in lumps of the size of a hen's egg, from 95 per cent of coal dust, 5 per cent of clay, and a binding substance made from rye flour and slaked lime. Subsequently the lumps are soaked with paraffin

¹ "Zeits. f. d. chem. Grossgew.," v. Post, 1877, 1.

residue dissolved in benzine, in order to protect them from the weather. The clay is dried on iron plates over a movable fire and ground, then mixed with sieved coal dust by means of a special appliance, which measures off the necessary quantity of each constituent, and delivers them into a receiver, where they are mixed with the binding medium which drips over them. In a second large iron tank the mass is kneaded between iron rollers covered with teeth; it then goes to the hopper of the press, the two rollers (29 ins. in diameter) of which are each hollowed out into 870 large and 56 small moulds. When the moulds meet in the rotation of the rollers, the soft mass is pressed in, and falls in egg-shaped lumps upon a moving band of woven wire. The large lumps weigh 3 oz., the smaller about $\frac{1}{2}$ oz. They are dried on moving woven wire belts in an oven at 250° C., and then fall on to another belt with wire sides which carries them through a bath composed of paraffin residues and benzine. The volatile benzine is then distilled off in the "evaporator," when the briquettes are ready for use. The apparatus turns out 150 tons of briquettes daily. The product is considerably cheaper than ordinary coal.

Briquettes from Lignite.—At the lignite mine at Frielendorf, near Cassel, in 1876, a new briquette works was erected,¹ the arrangement of which was as follows: The lignite was drawn up from the bottom of the open working in half-ton wagons in a winding shaft, by means of steam power, to the top, whence it was transported on a covered tramway, either to the hoppers from which the boilers were fed, or to the hoppers of the rotatory sorting apparatus, and there emptied out. A short screw conveyer carried the lignite, which was to be compressed, to a sorting cylinder, which passed all the pieces above 7 mm. partly through the large openings in the latter half of the sieve, and partly through the end of the cylinder, whence they fell upon a pair of rollers below. The material, which was here ground below a maximum size of 7 mm., together with the small which had fallen through the finer part of the

¹ "Preuss. Zeits. f. Bergwesen," 1876.

sieve, passed into a horizontal screw conveyer, which now carried the fine coal to an elevator. The latter raised the coal through a height of 8 ft. to a horizontal screw conveyer, passing over the drying-ovens, which were thus furnished with the necessary quantity of moist ground lignite. After the material had passed through the interior of one of the four sections of the automatic oven, and had left the delivery apparatus, the now dry coal was taken by an elevator, cased with sheet-iron, to the level of the hoppers of the two presses, from which it fell spontaneously through a regulator, and finally left the presses in the form of briquettes. These now went to a wooden trough, through which the machine forced them in a compact string, into the store to be stalked, if they were not loaded for transport direct from the trough. The presses did not differ materially in construction from other coal presses which have recently been found satisfactory. Each consisted essentially of a thirty horse-power horizontal engine, together with the stamp and the press head, which was rigidly connected with the bed-plate of the engine. The press head—a cast-iron cube—carried the orifice through which the lignite was supplied, and was traversed by a chamber 62 ins. long, containing the press feeder, which consisted of top, bottom, and two side wedges, between which the stamp moved and effected the compression of the material. A wrought-iron plate resting upon the upper wedge, pressed by a screw at the front, and moving on a strong spindle, served to close the top of the press chamber and to regulate the pressure or friction in the mould. The lignite already in the press chamber, which had been solidified, provided the resistance for the next following briquette. At both sides of the press block were hollow pieces, through which hot steam was sent to heat the block. The compressed lignite, as previously remarked, from the press entered a wooden trough in front in a continuous stream, and was then pushed outside the building into wagons, or to the store. Without overloading the machine, the stream of briquettes might be from twenty to forty yards long. One great advantage of the

Frielandorf apparatus, as opposed to the ordinary trough and plate machine, was that, within the former, there were no moving parts, which in the latter cause so many stoppages and repairs, and also give rise to the formation of much dust and danger of explosion.

Compressed Fuel from Lignite-coke and Peat.—F. Mathey states that a compressed coal may also be made from lignite-coke and peat; yet these require a somewhat greater addition of saltpetre than charcoal. The latter, obtained from different works, contained 2-4.5 per cent of potassium nitrate.¹ The Chemnitz works use as binding medium gum-arabic waste; Knorr, of Weissenfels, uses rye flour; others, dextrine. Of gum-arabic, as much as 4 per cent is added; of dextrine and rye flour, 4.8 per cent. Instead of rye flour, gluten—a waste product of starch-works—would be better.

Practical Experiences in Briquette-making.—At the Aix District Association of German Engineers, Hilt read a paper concerning the local development of the briquette manufacture.² In the first place, he maintained that this industry could only take root where small coal was to be obtained at one-quarter of the price of large coal. Coking is the best method to use with very bituminous small coal. For briquetting the small of non-caking coals, there may be used—(1) mineral binding agents, such as clay, loam, gypsum, cement, and lime; the resulting coke naturally contains much ash and is not hard; (2) carbonaceous binding agents, such as glue, starch, tar, and coal-tar pitch. The briquettes obtained are impervious to weather, may be readily transported or stored without crumbling, and possess a heating effect similar to that of large coal. The first species of briquettes, made with mineral substances, is much used for domestic purposes, but is unsuitable for boiler firing. The second kind, made with organic substances, may also be used as boiler fuel, with a good draught and care in firing, without producing excessive smoke.

¹ "Deutsche Industrie-Zeitg.," 1876, p. 125; "Dingler's Journ.," 1878, p. 90.

² Wieck's "Gwb.-Zeitg.," 1878, No. 39; "Zeits. f. d. chem. Grossgew.," v. Post, III, 1, 1878.

The somewhat slow combustion of these briquettes may be counteracted by using a thicker layer of fuel, by breaking them up, and by more frequent raking of the fire. In making the briquettes the coal and binding medium are mixed in the proper proportions in a suitable apparatus, provided with a mechanical stirrer, in which the mass is softened by hot air entering the apparatus or by heated steam. The briquettes are then moulded, under a high pressure, in closed moulds, or in an apparatus similar to the well-known brick press.

Drying apparatus for briquettes has been made of many forms. Most of these considerably increase the cost of manufacture. The cheaper drying apparatus of A. Wilcke is here described.¹ Upon a solid foundation, 3.25 metres (12½ feet) square, in which are two flues for supplying and removing the heating gases, are built two walls containing flues, 1 metre (39 ins.) thick and 1 metre apart. Between these two walls floors are built in, consisting each of two iron plates, which floors are closed at the short ends by plates, so that the fire gases introduced by the flues into the closed boxes must heat the plates. Thus, when the flues are connected to a fire, they bring the gases to the second floor, which they pass through, then through the third, and so on, until they are drawn off to the chimney and reach the atmosphere. If eight such floors, each 3 metres long, are placed one above the other, the fire gases have an opportunity of giving up their heat to the 24 metres length of iron plates which they touch, to the full extent allowable in view of the necessity of producing a sufficient draught in the chimney. The gable-ends of the iron floors are protected from cooling in a suitable manner. The separate floors are so arranged as to project in turn, so that the projecting part catches the coal falling down from the floor above. Similarly, in order to shut off the open space between the separate floors from the outside, movable flaps are provided. The upper plate of each floor is surrounded on three sides by a ridge; on the open side the coal is brought down to the next floor. Thus, as stated above, the coal goes from

¹ "Dingler's Journ.," 221, p. 523.

floor 1 to floor 2; the narrow edge of floor 2, protected by the ridge, projects 250 mm. (10 ins.) beyond floor 1. If now some arrangement be provided by which the coal, which reaches floor 1 from a hopper, is moved over the plate of floor 1 to that of floor 2, and so on, and if this motion be so regulated that the coal is heated to about 60° C. when it arrives at the delivery-shoot, coal quite suitable for briquetting will be obtained.

The movement of the coal over the plates is accomplished by means of a lattice provided with scrapers, and moved by mechanical power. Two \perp -shaped rails are connected by two cross-bands and two transverse rails; this grating is provided on the flat under-surface with flat scrapers 100 mm. (4 ins.) apart, and is coupled to cranks on the shafting. When the shaft rotates, the grating is moved backwards and forwards over the plates. This motion to and fro would, however, not move the coal lying on the plates, which can only be done if the grating, in moving back, is raised over the coal without touching it. Projecting pieces are arranged on the shaft, which act so as to raise the grating in the reverse movement. This rise is naturally at first gradual, so that the scrapers level the ridges into which the coal was brought in the forward movement. Thus the coal is stirred, which is a necessary condition for the uniform drying of coal intended for briquettes. The grating is supported by a foot running on a small wheel, so that it may keep at the greatest height until the end of the reverse stroke; when the reverse stroke is finished the grating falls, and then again moves the coal forward.

The rails run upon rollers, in order to prevent the scrapers from grinding on the plates during the forward movement, and stays are used in the floors to prevent the plates from buckling. The grating also runs upon three wheels in the middle.

If now coal is continuously brought upon floor 1 from the hopper, when the grating is put in motion the coal is regularly moved forward. As soon as the grating commences

the retrograde motion a valve closes the hopper, and feeding ceases until this motion is finished. If this were not done, too much coal would be piled up in the hopper, and some would be thrown over the edge. The coal is gradually carried over floor 1, then falls to floor 2, and so on, until it finally reaches the press, whither it is carried by elevators or conveyers. During the passage of the coal it is uninterruptedly exposed to the heat radiated by the plates, which is prevented from escaping too rapidly by the flaps before-mentioned. The fresh coal is subjected to the greatest heat, since the fire gases are conducted into the apparatus from above.

Clayton has constructed a machine for compressing small coal into briquettes.¹ A horizontal plate carrying moulds of the required size is placed between two cast-iron columns. Upon the plates moves the filling-box, to which the material, prepared in the proper manner, is conveyed from the mixing-drum. The filling-box obtains its movement to and fro by means of a bent lever from the cross-head. The briquettes are compressed from two opposite sides. The lower pistons are driven by cogs on the wrought-iron shaft supported by the framework. The upper pistons of the press are actuated from the shaft by cranks and strong connecting rods, suspended from the cross-head which moves in the framework. In order to avoid excessive pressure on the mechanism, the upper pistons are provided with strong springs.

When the moulds are filled with coal, the upper and lower pistons at once move and compress it to a solid brick. The upper pistons then rise, and are followed by the lower pistons, the finished briquette being thus raised out of the mould to the level of the plate. The filling-box in its return with fresh material removes the briquette. The reversal of the lower pistons, which also affect the lubrication of the moulds in a well-known manner, is brought about by cog-wheels on the shaft.

A two horse-power steam-engine is sufficient to drive a press which can produce per day about 10,000 briquettes.

¹ "Dingler's Journ.," 203, p. 271.

each weighing 5 lb. The space required is very small; a ground space 5 ft. long by 4 ft. wide, with a clear height of 6 ft., is sufficient.

Finally, E. F. Loiseau has constructed a machine for converting anthracite dust into an artificial fuel.¹ The coal dust is moistened on a platform and then scraped into the hopper of a stationary cylinder, in which a shaft rotates. On the shaft are six radial plates which divide the interior of the cylinder into six equal spaces. The coal dust fills these spaces, and the rotation of the plates drives it into an opening beneath, through which it leaves. A smaller hopper, placed close against the first, receives clay previously dried and ground. This passes through a smaller cylinder, also provided with rotating partitions, and is then emptied into the same channel as the coal dust, with which it mixes.

The space between the partitions of the clay cylinder is calculated regularly to take and deliver 5 parts of clay, whilst the larger cylinder delivers 95 parts of coal dust. The mixture of coal and clay is sprinkled with milk of lime whilst it is falling below a chain elevator, which now raises the moist mixture to the hopper of a conveyer. The Archimedean screw rotating in the latter drives the material into a mixing apparatus, where it is rapidly transformed to a plastic mass by means of seven vertical shafts, to each of which four toothed arms are screwed. These arms cross one another in all directions, and intimately mix the coal and clay together. Through suitable openings at the bottom of the mixer, the plastic mass falls along a shoot into the kneading machine, in which, by a series of knives attached to the central shaft and a propeller, it is forced through an opening at the bottom between two rollers, in the periphery of which are a series of oval moulds. These rollers, moving in opposite directions, take the material presented to them in the form of a coherent band, and mould it into oval lumps. An endless wire band

¹ "Journ. Franklin Institute," 1873, p. 266; "Dingler's Journ.," 210, p. 437.

carries the lumps away, and delivers them into a hopper placed above the drying-flue.

The drying-flue is heated from a fireplace at each end. It contains five endless wire belts, one above the other, which move in opposite directions over rollers placed at the ends of the stove, and which have an arrangement for preventing the lumps from falling down. The compressed lumps of coal fall upon the topmost wire belt, are carried by it through the whole length of the stove, and then slide along a shoot which carries them on to the second endless belt beneath. This belt carries them in the opposite direction through the whole length of the flue to a second shoot, from which they pass down to the third belt, upon which they are carried forward, and so on. The last wire belt carries the coal out of the stove and empties it into the buckets of an elevator, by which it is raised and then delivered to another endless band, which passes through an open tank, fed continuously from a neighbouring larger tank, by which the smaller tank is kept filled with the waterproofing composition. The endless band is provided with small partitions, which prevent the oval lumps from suddenly falling down into the composition. The continuous immersion of the coal in the waterproofing mixture is brought about by small balls at each side of the belt, which run in narrow grooves on the walls of the tank. On leaving the tank the excess of liquid drips from the lumps of coal through the wire belt into a gutter beneath, from which it flows away by a pipe to a convenient tank.

The waterproofing composition employed by Loiseau is a solution of colophony or some other resin in benzine. In order rapidly to evaporate this benzine, the lumps of coal coming from the bath are emptied into the hopper of a stove of smaller dimensions than the drying-flue, in which only three endless belts are placed one above another. In this flue a strong current of air, driven by a fan, rapidly evaporates the benzine, whilst the coal goes from one belt to another. From the last belt it falls through a shoot into the coal truck outside. The end of the shoot may be raised so

that a filled truck may be taken away and an empty one brought in its place.

During the passage of the material through the flue the hot air acts on all the lumps and rapidly dries them. The whole process of manufacture, from the passage of the coal dust into the first hopper, proceeds automatically; coal dust and clay are mixed in the proper proportions with milk of lime, this mixture is kneaded, compressed into oval lumps, which are dried and waterproofed, the benzine is evaporated, and the finished products delivered to the trucks, all mechanically. During the whole process the coal is continuously in motion.

CHAPTER XXXVI.

ILLUMINATING GAS FROM WASTE AND THE BY-PRODUCT THE MANUFACTURE OF COAL GAS.

*Utilization of Waste Products in Making Illuminating Gas from Suint.*¹—In addition to the waste products containing fat—bones, oil-cake, etc.—soap waters—produce washing the grease out of wool and the gum from silk—be used with advantage for the production of an illuminating gas. It contains the original grease of the wool, oleates and stearates of soda and lime, and also nitrogenous organic matters from the wool and silk. The fatty acids separated from the suds either by inorganic acids, or they are combined with lime and the product subjected to distillation. (a) *Distillation of the separated fatty acids.* According to Knapp, at Rheims, 300 cwt. of wool-wash suds are mixed with 2 per cent of sulphuric acid and 1 per cent of hydrochloric acid and equal quantities of water and allowed to stand for twelve to eighteen hours, when the impure greyish mass of fat which has risen to the surface is mechanically cleaned, melted in a copper boiler and, whilst fluid, treated again with 2 per cent of sulphuric acid. The clear oil obtained is used for soap-making and the black, solid, fatty residue employed for producing gas. The tar which separates in the distillation is always again used to dissolve the solid residue. (b) *Distillation of the separated lime soaps.*—At the spinning-mills in Mühlhausen and Augsburg, according to Altgelt, the wash containing the sweat of the wool and the used soap is allowed to stand with milk of lime for twelve hours, when the clear liquid is drawn off, the deposit sieved through a

¹ "Dingler's Journ.," 195, pp. 175, 216, 517.

linen cloths, and the mass which passes through allowed to stand for six to eight days in a cellar until it forms a pasty mass, which is then cut up with a spade into rectangular lumps of the size of half a brick. These lumps are dried for several weeks on frames, and the dried mass, which is termed *suiter*, subjected to distillation. A gas is obtained which it is not usual to purify, and which has three times the illuminating power of coal gas. The soap liquors in which silk has been boiled, according to Jeannency, are heated with slaked lime to 70-75° C., allowed to clarify during two to three days, the clear liquid decanted off, the deposit filtered, spread out to dry in the air, and then used for gas-making. One hectolitre (22 gals.) of the soap liquor requires 0.75-1.5 kilo (1.68-3.37 lb.) of quicklime, and gives 1200-1600 litres (42-56 cub. ft.) of gas. The gas is not purified or washed, but is taken direct from the retorts to the gasometer.

Illuminating Gas from Wool Waste.—Liebau, of Magdeburg,¹ employs wool waste from spinning mills either alone or, better, mixed with coal to produce illuminating gas. A layer of coal 52 mm. deep (2 ins.), then a layer of wool waste 157 mm. (6.3 ft.) deep, and finally a little more coal, are brought into the scoop used for filling the retorts, and the contents quickly emptied into the retort, which is at a low red heat. With a retort of 30 kilos (67 lb. capacity) the distillation is finished in one and a half to two hours. Fifty kilos (1 cwt.) of waste produce 21.63 cub. metres (800 cub. ft.) of gas, whilst the coal also gives about 17 cub. metres (630 cub. ft.) of gas per 50 kilos (1 cwt.). The carbonic acid is removed by purifying. It is advisable to use the wool waste mixed with coal rather than alone, since a saleable coke is produced, the cheaper clay retorts can be used, and the purification is also less expensive.

*Illuminating Gas from Beet Molasses, Wine Lees, and Grape Marc.*²—From 100 kilos (2 cwt.) of dried, or 111 kilos (250 lb.) of crude molasses, Stammer has obtained

¹ "Dingler's Journ.," 184, p. 380.

² "Deutsche Industrie-Zeit."

61.8 cub. metres (230 cub. ft.) of unpurified illuminating gas. The residues from the maceration of dried beet, after pressing and drying, give 24.72-37.08 cub. metres (916-1375 cub. ft.) of gas per 100 kilos (2 cwt.). The gas contains 23-24 per cent of carbonic acid. Three kilos (6½ lb.) of 10 per cent ammonia liquor or 1.2 kilos (2.6 lb.) of sulphate of ammonia are also produced.

The grape marc, which has already been used for producing tartaric acid and marc brandy, may further be used with profit for gas-making.¹ No other appliances are necessary for producing gas from the grape marc than those used for coal or wood gas. Grape marc may therefore be treated in any well-arranged coal-gas works. The by-products obtained by condensation from the gas produced by grape marc are essentially the same as those obtained from wood gas, viz. acetic acid, ammonia solution, and a mixture of hydrocarbons similar to wood tar, which may very well be utilized for the preparation of creosote, photogene, and paraffin. It is absolutely necessary that the marc used for producing gas should be free from alcohol, i.e. only marc can be used from which brandy has been prepared or from which the alcohol has evaporated by long lying in the air; it must also be air dried, and should not be mouldy. The marc, as it comes from the brandy distillery, is pressed in order to remove the greater part of the liquid. It is then dried, for which purpose it is pressed into moulds, which may be either rectangular boxes, open at top and bottom, or circular rings; rectangular bricks or round cakes are thus produced in the same manner as the bricks of tan-bark. The bricks or cakes are quickly dried in the open air on hurdles or frames. Drying the marc by the aid of artificial heat is not advisable, since if the drying be carried only a little too far, not only is much less gas obtained, but also gas of lower illuminating power. The dried bricks may be kept for years before use, if they are piled one above another in open layers so that the air can always pass between them. The retorts are charged

¹ "Die Verwerthung der Weirückstände," A. dal Piaz, Vienna.

in the same manner as with coal. At each charging 20-50 kilos (42-112 lb.) of the marc bricks are introduced, according to the size of the retorts, so that five- or six-tenths of the internal volume is occupied. The quantity of marc cakes required for one charge is distributed in a charging scoop, of the same length as the retort and of semi-circular section. The scoop is then quickly pushed into the retort and turned over, so that its contents are emptied on the bottom of the retort. The empty scoop is rapidly withdrawn and the retort lid, the edge of which is well smeared with clay paste, screwed on. When the retort is closed a violent distillation and evolution of gas take place as soon as the retort is sufficiently heated. As in making wood gas, a charge of grape marc is completely gasified in two hours at the most, whilst coal requires five to seven hours before it is entirely exhausted. The treatment of the grape marc has thus the advantage over that of coal that a large quantity of gas can be rapidly made without large furnaces and gasometers being necessary. The gas is also of greater illuminating power than ordinary coal gas, but particular care has to be taken that the grape marc used is thoroughly air dried, and quite free from alcohol and mould. If the intention in gasifying grape marc is to obtain good Frankfort black, then no higher temperature is used in the distillation than is required to maintain the retorts at a dark red heat. Thus it is advisable to use for heating the retorts or gas furnaces, in place of the usual coke, a fuel of less heating power, such as turf, lignite, or wood, especially when coke is the more valuable. When grape marc is gasified with the retorts at a dark red heat, a coaly residue of a dull, deep bluish-black colour is obtained, which produces Frankfort black of a very fine shade. If, on the contrary, the retorts are almost at a white heat, the residue is dark grey and shining like graphite, to which when ground it is quite similar; it may be used ground in linseed oil as "furnace black," a greyish-black paint of good covering power.

After the distillation has continued one to two hours, ac-

ording to the size of the retorts, the evolution of gas slackens, the gasification of the charge is then regarded as finished, and the hot residue at once withdrawn from the retort. When the retort lid is opened, the gases issuing from the retort are lighted, as in making coal gas, in order to avoid an explosion. The withdrawal of the red-hot charge, similarly to the charging, is carried out as rapidly as possible, in order that the residue may not be partially burnt, which would result in the product being contaminated with a fine white ash.

It is therefore necessary to use a broad rake in emptying the retorts, to rake the contents into a sheet-iron box with a well-fitting lid, placed below, and at once to close the box with the lid in order to exclude the air. It is, however, better and simpler partially to fill the box with water, so that the glowing contents of the retort are quenched immediately they are drawn.

In making gas from grape marc similar condensing apparatus is required to that used for coal or wood gas; as with the latter, dry lime is used for purifying. The gas lime obtained in the purification, and also the other by-products of the condensation, can be utilized in the same manner as those obtained from wood gas or coal gas. Experiments made at the Grünstadt gasworks have shown that when the retorts are almost white-hot, from a 50 kilo (1 cwt.) charge of completely air-dried grape marc about 17.5 cub. metres (648 cub. ft.) of gas are obtained of a considerably higher illuminating power than ordinary coal gas. At a dark red heat the yield of gas is smaller—thus, from a 50 kilo charge, about 15.6 cub. metres (577 cub. ft.) of gas of the same illuminating power as ordinary coal gas are obtained.

The grape seeds, separated from the marc and dried, in consequence of the oil they contain, yield almost twice as much gas as the marc, this gas far surpassing that from marc in illuminating power. The carbonaceous residue obtained in gasifying the seeds also gives Frankfort black. In gasifying grape marc the residue, i.e. the Frankfort black, amounts to one-quarter of the weight of the dried marc;

therefore it is possible to reckon with certainty on obtaining 20-25 per cent of grey or black pigment.

*Illuminating Gas from Fusel Oil.*¹—The fusel oil from potato spirit is generally preferred in the manufacture of perfumes to fusel oil from beet or molasses distilleries, since it contains more amyl alcohol. H. Briem recommends that this by-product of the molasses distillery, which has little commercial value, should be used for preparing illuminating gas, for which purpose it is passed through a heated pipe. The iron pipe required for decomposing the fusel oil has a diameter of about 10 cm. (4 ins.) for lighting 100-200 burners; it is laid in the fireplaces of the furnaces used for evaporating the wash.

Illuminating Gas from Sewage Deposits and Excrement.—The first experiments with this object date back to 1827, when Reimann, of Berlin, made illuminating gas from faeces. The price of the new gas was, however, higher than that of coal gas, and thus this method of utilizing excrement had to be abandoned. Of the more modern processes, two in particular are worthy of notice: the first, for the production of illuminating gas and hydrogen from sewage deposits, is due to R. G. Hickey; the second, of illuminating gas from excrement, to Sindermann, of Breslau.

Hickey has published a description of this process,² according to one modification of which hydrogen, for illuminating purposes, is obtained by passing superheated steam over sewage deposit, heated in a retort. Another modification consists in producing a gas for lighting and heating from sewage deposits. Hickey intended to make excrement of all kinds innocuous in this manner, by carbonizing it in closed retorts, and using the residue in the retorts for removing the smell of fresh matter before its introduction into the apparatus, and also, together with the distilled products, as manure; the gas was to be used either

¹ "Zeits. d. Ver. f. Rübenzucker-Industrie."

² "Dingler's Journ.," 195, p. 378.

for lighting or heating, or for both purposes. The process differs somewhat according to the result desired. For the transport of the sewage deposit to the gasworks, buckets of circular or elliptical section are used; they narrow at the top to a neck from 3-4 in. wide, which is filled with the ignited excrement, and may also be closed by a water-lute, to prevent the escape of smell. The fluid constituents are partially removed from the matter before it is brought into the retorts, and are also made odourless by means of the ignited residue. For this purpose the mixture is brought into a cylinder with a perforated bottom, covered by a layer of ignited residue. When full, a tight-fitting plate is laid on at the top, and then, by a screw mechanism, a gentle pressure is applied, which expresses a large part of the liquid in a completely innocuous condition.

The retorts in which the pressed matter is heated are either of clay or wrought iron; they are best \square -shaped, and have at each end an opening, closed during use by a tight-fitting lid, smeared with clay; the retorts are laid at an angle of 15-20°. If the gas is to be used for heating only, the gases and vapours are allowed to rise through pipes, and then through a water-tank divided into several compartments; in this manner they are completely washed, and the ammonia salts mostly separated. The gas then passes through a condenser, and thence into a small gasometer, from which it passes through a pipe, furnished with a regulating valve and ending in a head provided with slits, to the furnace, where it is burnt with the addition of partially carbonized excrement. If the gas is to be used for lighting it requires to be more carefully purified. It leaves the retort, as does coal gas, to enter the main pipe, which must be of relatively large size; it goes thence to the condensers, in which the ammonium and other salts are removed by repeated passage through water. It then goes through a scrubber—a cylinder filled with bricks, stones, charcoal, or large lumps of the retort residue—and finally through a dry purifier, which contains alternate layers of lime and retort residue, spread on

frames one above another, which it leaves for the gasometer.

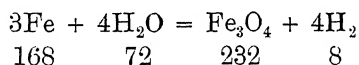
If the gas produced in the retorts is to be used for heating, and, at the same time, hydrogen gas is to be made for lighting purposes, the gas which is first evolved is conducted away, as in the first case; as soon as the evolution of gas has ceased, the connection with the pipes leading to the condenser is cut off by a tap, and then superheated steam, from a small boiler built in the furnace, and which may be fed with the liquid expressed from the excrement, is passed through a perforated pipe over the red-hot residue in the retort. Pure hydrogen and carbonic acid are formed almost entirely; the latter is removed in a dry lime purifier, whilst the hydrogen is burnt in an Argand burner, provided with platinum gauze.

The gas produced from human excrement burns with a very bright flame. The residue remaining in the retorts is an odourless black powder, which is very suitable for removing the odour from solid and liquid sewage matters, and, like the deposit in the condenser, produces an excellent manure. From the liquid condensed in the main pipe, by evaporation with hydrochloric acid in pans on the top of the furnace, sal-ammoniac is obtained in large quantity.

A very favourable report on Sindermann's process was given in 1875 by the Breslau Common Council, which had appointed a special commission to examine it. The fæces are brought in small quantities—with the apparatus then used 2-3 kilos ($4\frac{1}{2}$ - $6\frac{1}{4}$ lb.)—every fifteen to twenty minutes into a heated retort. One hundred kilos (2 cwt.) of fæces require 50 kilos (1 cwt.) of coal, and produce 7.8-9 cub. metres (290-333 cub. ft.) of gas, and with the addition of 1 kilo ($2\frac{1}{4}$ lb.) of iron turnings, 24 cub. metres (888 cub. ft.) of gas. In addition, there are said to be obtained—6.66 kilos (15 lb.) of coke, which may be used as manure; 3.33 kilos (7.5 lb.) of tar; 3.33 kilos of fat, which is used for protecting the collecting barrels; and large quantities of ammonia liquor.

The process just described can hardly exist in actual

practice; in a critical examination by Fischer,¹ it is entirely rejected. Therefore it may here be mentioned that, according to Gintl, fæces contain an average of 92.5 per cent of water and 1.6 per cent of ash. Thus, in order to obtain 5.9 kilos of organic matter, from which gas can be made, 92.5 kilos of water have to be evaporated, which again must be condensed in a gigantic cooling apparatus. Whilst a coal-gas works consumes barely half the coke it produces from the coal, in treating fæcal matter large quantities of fuel must be purchased. The production of larger quantities of gas by an addition of iron turnings can, at least in substance, only result from the decomposition of water by heated iron. Now



therefore 168 kilos of iron give 8 kilos or 89.5 cub. metres of hydrogen; thus 1 kilo of iron, even when it is completely transformed into Fe_3O_4 , can only give 0.5 cub. metre. Sindermann's statement, that an addition of 1 per cent of iron turnings can increase the yield from 8.24 cub. metres, must therefore rest on error. The gas liquor will, as a rule, barely contain 0.5 per cent of ammonia, and is therefore far more difficult to utilize than that from coal. Also, the tar and the fat apparently obtained seem to have a low value. Since, further, the tending of the apparatus requires relatively much labour, the process cannot be profitable.

Utilization of the Ferric Oxide Used for the Purification of Coal Gas.—Various methods have been proposed. According to an English patent of H. Grüneberg, the spent purifying mass, after extraction with water and alkali, is treated with hydrochloric acid in order to separate part of the sulphur, and is then converted into Prussian blue by means of a ferric salt and bleaching powder.²

Gerlach proposes to grind the purifying mass fine, and then to extract first with water, next with caustic soda solu-

¹ "Dingler's Journ.," 217, p. 425.

² *Ibid.*, 227, p. 212.

tion. From the last extract, sulphur and cyanides are precipitated on the addition of acid to slight acid reaction; ferric chloride is then added to the solution, drawn off from the precipitate, and filtered if necessary. The residue remaining after the two extractions yields its sulphur on distillation in an iron or clay retort in a current of superheated steam. The extracted and desulphurized mass is converted into colcothar by heating with access of air.

P. Spence uses the following process: The spent iron oxide is first washed with water in a suitable tank, in order to remove any ammonia compounds present. The mass is then again dried in the air, a quantity of quicklime equal to half the weight of the oxide is slaked, and the dry hydrate intimately mixed with it. The mixture is lixiviated with warm water—not above 70° C.—in iron vessels with double bottoms. The solution when slightly acidified gives, with ferric chloride, a precipitate of Prussian blue. This precipitate is used as such, or employed to prepare yellow prussiate of potash. After the ferric oxide has given up all the potassium ferrocyanide, it is heated in the same vessels with water to boiling. A solution of calcium polysulphides is obtained, from which hydrochloric acid precipitates sulphur. The ferric oxide thus extracted is again used for purifying coal gas.¹

The oxide used for removing the sulphur from coal gas is a natural hydrated oxide of iron, known as bog iron ore, containing about 30 per cent of ferric oxide or an artificial product known as "Lux" prepared from bauxite. Sometimes Weldon mud or impure hydrated oxide of manganese is used in place of it. When a purifier shows that sulphuretted hydrogen is ceasing to be absorbed it is thrown out of the series, opened up, and the oxide of iron removed. On exposure to air rapid oxidation takes place with re-formation of oxide of iron and liberation of free sulphur. It is used in this way again and again until it contains about 50 per cent of free sulphur, when it is sent to the sulphuric acid works

¹ Eng. Pat. 4118; "Chem. Centralblatt," 1879, No. 28.

and burnt for the production of sulphur dioxide in a similar manner to iron pyrites.

In small gas works the sulphuretted hydrogen is absorbed by lime, forming sulphide of lime, from which the sulphur cannot be removed, but this also has a use, as it can be employed by farmers for digging into the land as a dressing for crops, in place of quicklime, and is no doubt of benefit in destroying insects and worms.

Prussian Blue from the By-Products of the Manufacture of Coal Gas.—According to the English patent of Valentin, ferric hydroxide, which has been used for purifying coal gas, is washed with water, digested with magnesia or chalk at a high temperature, and then extracted with water. The pale yellow, somewhat alkaline solution contains calcium or magnesium ferrocyanide; on the addition of a little acid and an iron salt it deposits fine Prussian blue.

Treatment of the Used Laming's Mixture of the Gasworks.—For many years the chemical works of Kunheim, Berlin, have worked up the Laming's mixture from gasworks.¹ The mixture of ferric oxide and lime, which are the essential constituents, soon absorbs a large quantity of ammonia, sulphur, and cyanogen compounds. By washing with water the ammonia salts are extracted and isolated. The residue, when decomposed with lime, gives a soluble double cyanide, from which yellow prussiate of potash may be obtained by precipitation with potassium sulphate. The insoluble portion, when roasted, gives up the whole of its sulphur, which is utilized in vitriol chambers; there remains ferric oxide in a condition very suitable for the purification of gas. In addition, ammonium sulphide, and, by direct treatment with hydrochloric acid, Prussian blue may be prepared.

There are two methods of extracting the cyanogen from coal gas in successful working, the first being that introduced at the Beckton gasworks in 1892, in which the gas is washed by passing it through a solution of ferrous sulphate

¹F. Beilstein, "Die chemische Grossindustrie"; "Dingler's Journ.," 211, p. 76.

or of sulphide of iron suspended in water. In this way the bulk of the cyanogen removed is obtained as ammonium ferrocyanide. In Germany a similar process was patented by J. Bueb, but the process is carried only so far that the cyanogen compounds are left in an insoluble form in the sludge from which they are subsequently recovered.

The polysulphide process depends on the fact that ammonium polysulphide formed by treating spent oxide with ammonium sulphide absorbs cyanogen yielding ammonium cyanide, ammonium sulphocyanide, and ammonium sulphide. This process is due to the British Cyanides Company, and also to P. E. Williams, who patented it in 1909.¹

Recovery of Sulphur from Laming's Mixture.—The sulphur deposited in the mixture may either be extracted with carbon bisulphide, or may be industrially utilized by burning the mixture in the sulphur burners to sulphur dioxide, when 1 ton produces 1½ tons of sulphuric acid.² G. Pelouze recommends to utilize the solubility of sulphur in coal-tar oils for its extraction from Laming's mixture.³

Simultaneous Utilization of Coke Dust and Gas Tar.—In large gas works coke dust is produced in considerable quantities; it has hitherto been utilized only by a somewhat laborious process with little profit. It is mixed with small quantities of coal tar, or tar freed from its volatile constituents by distillation, or even with loam or clay, and moulded into briquettes by special machinery. The briquettes form a good fuel, but they require to be made by powerful machinery, and are consequently expensive. Coal tar, in consequence of its chemical composition, is by itself a valuable raw material for the production of illuminating gas, but all attempts to utilize it in this manner have failed owing to various technical difficulties. The engineers of the Paris Gas Company have proposed to utilize coke dust and coal tar by the simultaneous production of a good fuel from the former and of illuminating

¹ "Lectures on Chemistry in Gas Works," W. J. A. Butterfield, Institute of Chemistry, 1913.

² "Dingler's Journ.," 196, p. 372.

³ *Ibid.*

gas from the latter by-product, and have obtained a patent for the process.

In any simple mixing apparatus, 50 parts by weight of tar are well mixed with 40 parts of coke dust, brought into the retorts by means of the ordinary semi-cylindrical scoop, and heated for three or four hours at a temperature of about 1200° C. After this lapse of time, the distillation of the admixed tar is finished, and the solid coked residue has sintered with the coke dust to a solid mass, which has only to be cooled by water or steam and broken up, in order to yield an excellent fuel, burning readily in a grate with a slight draught, and especially suitable for household use, etc.¹

Utilization of Lignite Coke.—It is well known that, in the dry distillation of lignite, coke is obtained in considerable quantities as a by-product which is difficult to utilize. Formerly it was only applied as road material, but later² it has begun to be used in the so-called ashpit stoves. The "Wochenschrift für Oel- und Fettwaarenhandel" calls attention to other uses for this by-product. Coleman has (loc. cit.) made successful experiments with a view to using lignite clinker for disinfecting the latrines of two large hospitals in Glasgow. Two parts of the contents of the latrines, mixed with one part of bone-black or powdered lignite coke were temporarily, and when mixed with an equal quantity permanently, deodorized. Coleman accordingly proposes to use lignite coke for disinfecting the contents of the sewers of towns and to utilize the product as manure.

There have also been several communications in this connection to the "Zeits. f. Paraff." in regard to the utilization of the lignite coke of oil distilleries for the same purpose, by the use of which equally favourable results have been obtained. However, more may be expected from the application of lignite coke as fuel, if only suitable fire grates can be constructed for the purpose.

¹ Armengaud's "Publication industrielle," 22, p. 491; "Dingler's Journ.," 219, p. 470.

² Post's "Zeits. f. d. chem. Grossgew.," III, 1.

regard to working up the tar, which is an industry in
d to describe which would be to overstep the limits
work, the reader is referred to the excellent and
work of Dr. J. Bersch, "Die Fabrikation der Anilin-
s," Hartleben, Vienna, and to Dr. Lunge's work on
ar and Ammonia".)

CHAPTER XXXVII.

BY-PRODUCTS IN THE TREATMENT OF COAL-TAR OILS.

It would be impossible in a single work to give details of the methods employed in treating coal tar for the recovery or production of the whole of the valuable substances. By simple distillation it is separated into benzene, toluene, carbolic acid, neutral tar oils, naphthaline, anthracene, and pitch or coke.

From it are obtained various grades of carbolic acid ranging from the common brown disinfecting fluids to the perfectly pure medicinal phenol. From phenol is obtained picric acid and from toluene is obtained trinitrotoluol, which are amongst the best of the modern explosives.

By various processes are obtained an enormous number of dyes derived from aniline and other coal-tar bases, from phenol, naphthalene, anthracene, naphthols, etc., besides which we have a whole range of synthetic perfumes and drugs.

Blast-furnace tars and also coke-oven tars are similarly treated for the production of oils and disinfectants, pitch and other products.

Coal tar and pitch are largely used for paving purposes in the production of artificial asphalt, and also in the newer tar macadam. The oils obtained from tar are employed in enormous quantities for creosoting or preserving timber.

Utilization of the By-products.—The caustic soda solution used in refining oils containing creosote is partly used directly as soda-creosote for impregnating mine timbers, and is partly worked up into carbolic acid. For this purpose the liquors are mixed with the sulphuric acid, which has

also been used for refining the oils, until the reaction is strongly acid. In this case, acid sodium sulphate is produced, which is more soluble, and hinders less the separation of the creosote than the more difficultly soluble neutral salt. The salt liquor is set aside to crystallize, and the separated salt sold to the soda or glass-works.

In decomposing with carbonic acid, which, according to L. Grotowsky,¹ is obtained from burning coal, the mixture of soda-creosote and water in equal parts must be cold. Carbonic acid is passed in until the liquid is saturated and froths up violently for about an hour. The separated soda solution is evaporated to dryness, ignited, dissolved in water, causticized with lime, the caustic liquor drawn off from the chalk mud, and concentrated to 35-38° B. The caustic soda solution thus obtained still contains impurities, and therefore can only be used to separate the creosote from crude oils.

The creosote, separated by one or the other process, after washing with water, may be brought into the market; it is used for soaking telegraph poles, railway sleepers, etc., also as a disinfectant. When distilled, it gives a fluid oil of 0.965 specific gravity with a strong odour, which is used as a disinfectant under the name of creosote oil, or in the manufacture of phenol dyes. By repeated solution in caustic soda, decomposition with sulphuric acid, distillation over iron filings, and finally over green vitriol, a quite white oil is obtained. The substance produced under the name of creosote by the mineral oil works in Saxony is, according to Grotowsky, simply phenol and cresol.

The acid resin drawn off from the refining apparatus is mixed with hot water in suitable vessels, and washed by direct steam; on standing, the empyreumatic resin separates out at the surface. The recovered acid, which is coloured black by organic matter, is sold at a strength of 40-50° B. to superphosphate works, where it is used for dissolving phosphates and bones. The resin is well washed, mixed with any un-

¹ "Zeits. f. Paraffin Ind.," also see p. 186.

utilized creosote, and subjected to distillation, when, according as tar or pitch is required, little or much creosote oil is distilled off.

The bone-black used in refining paraffin is boiled out with water, then heated in horizontal retorts to drive off the residual paraffin, and finally converted into superphosphate with the above acid.

CHAPTER XXXVIII.

AMMONIA RECOVERY.

Preparation of Ammonia Solution from the Ammoniacal Liquor of the Gasworks. The patented process of Watson was carried out in the following manner:¹ The crude ammoniacal liquor, together with a quantity of lime, which varies according to the quality of the liquor, is brought into a roomy retort or a boiler connected with a cooling apparatus. On warming, the gas is soon driven off, and is absorbed by the water in the receiver. On longer heating, much water distils over with the ammonia. As soon as this is observed, the receiver is changed and the later portions of the liquid caught separately, since the last portions are not alkaline, or only very slightly. This portion is brought back into the retort in a following operation, in order that it may be concentrated by a second distillation. The first portion distilled over is also not yet sufficiently pure; it generally contains certain oily substances which can be mechanically separated, and, in addition, a tolerably considerable excess of water; it must, therefore, be subjected to a second distillation alone. The ammonia gas is, as before, caught in a little water, and the receiver changed when too much water goes over with it. Thus a solution of ammonia is obtained, which is sufficiently pure for almost all technical operations. The second portion of the distillate is reserved for the next operation, when it is again brought into the still.

Concerning this process, Stohmann² remarks with justice that it is quite unpractical, since several distillations are required in order to produce a commercial product. This may

¹ Muspratt's "Chemie," 3rd ed., 1874, Vol. I.

² *Ibid.*

be avoided, he continues, by a methodical distillation, in which, during the operation itself, the quantity of ammonia contained in the vapours is increased, and the foreign constituents separated. The apparatus used for this purpose is really an improved spirit still.¹

Ammonia from Gas Liquor.—According to a patent of Braby and Baggs, ammonia is obtained from gas liquor by adding caustic lime, heating in a boiler to a temperature between 40° and 100° C., and then forcing air through a pipe reaching to the bottom of the boiler, the air being further distributed by a perforated bottom. The air, carrying ammonia and a little steam, leaves the upper part of the boiler and passes into a receiver filled with water, hydrochloric or sulphuric acid. At Deptford, where this process was employed, the air, laden with ammonia, first goes through a lime purifier containing milk of lime kept in constant motion by a stirrer, and then through a cooled coil to the receiver, which consists of three vessels. Two of these vessels are one-third filled with cold water, the last is filled with a strong solution of ferric chloride, which is converted into a solution of sal-ammoniac with precipitation of ferric oxide, which, after ignition, can be used as a painter's colour.

Ammonium Sulphate from Gas Liquor is made by P. St. Brown, in Ireland,² by incompletely neutralizing with sulphuric acid, thus leaving the liquor slightly alkaline, and evaporating in iron vessels until ammonium sulphate crystallizes out. The product is somewhat impure, and can only be purified by complex and repeated recrystallizations.

H. Krätzer has accordingly recommended a new method

¹ Newton used for this purpose, according to a patent in 1841, the still devised by Coffey, by means of which ammonia solution of any required strength, even to the strongest, can be obtained. Rose has also constructed an apparatus for the distillation of gas liquor. Compare Fleck, "Fabrikation chemischer Producte aus thierischen Abfällen," p. 150; Knapp, "Chem. Technologie," 3rd ed., Vols. I and II, p. 534; Muspratt's "Chemie," 3rd ed., Vol. I, p. 648.

² Post's "Zeits. f. d. chem. Grossgew.," IV, 1.

for the preparation of ammonium sulphate, which has been adopted in several chemical works, and which produces an almost completely pure salt. A little lime is added to the gas liquor in order to decompose the ammonium salts it contains; a rapid current of steam is then passed through the mixture. The whole of the ammonia is expelled, and when conducted into a water-tank gives at once ammonia solution of any required strength, from which by neutralization with sulphuric acid a product can be obtained far more pure than by previous methods. One hundred parts by weight of gas liquor give 1.2 parts of the salt. This method is particularly to be recommended to those works which make ammonium sulphate for use as a fertilizer, since the product is free from sulphocyanides and hence is harmless for agricultural purposes. Krützer showed, as a result of many experiments undertaken when director of the Agricultural Institute at Brandis, that sulphate of ammonia, made by older methods, generally contains ammonium sulphocyanide, and then injures the crops instead of improving them.

The following process¹ was patented in England by W. M. Brown, for J. H. Elvert, of Geneva, and J. J. M. Pack, of Basle, for the preparation of pure ammonia from gas liquor. The liquor is mixed in a closed vessel—cylinder or boiler—with the proper quantity of lime drawn off into a second vessel, and there heated. The steam containing ammonia, etc., is conducted to the bottom of the first vessel, which has meanwhile been recharged with gas liquor and lime, and from thence the gases, containing more ammonia, pass to a condensing chamber, from which the more readily condensable constituents flow back through a connecting pipe to the first-mentioned vessel, whilst the more volatile constituents pass through a cooling coil into a second condensing chamber, where hydrocarbons, sal-ammoniac, and a small quantity of free ammonia are retained. The purified vapours, consisting now almost entirely of ammonia, are conducted through several vertical pipes filled with charcoal and thence to

¹ Ber. d. d. chem. Ges., 1873, 1553.

receivers containing distilled water, which are changed as soon as they become saturated. As soon as all the ammonia has been driven out of still No. 2, it is emptied, filled with the contents of No. 1, the latter charged with fresh liquor as before, and the operation recommenced. Treated in this manner, 1000 litres of crude liquor at 3° B. give, in the course of from four to five hours, 100-110 kilos of commercially pure ammonia of 22° B.

The apparatus hitherto used for the distillation of the ammoniacal liquor of gasworks consists either of a still, in which the liquor is distilled alone or with lime, or two vessels are used, one of which serves to heat the charge, and the other serves as the still. If no lime is added, only the ammonia combined with volatile acids is obtained; in the other case the lime introduced into the apparatus causes danger of overheating the still, a danger only imperfectly removed by the introduction of a stirrer.

This evil is removed by an arrangement invented by H. Grüneberg, of Kalk, near Deutz,¹ which enables lime to be used without a mechanical stirrer, and thus brings about the recovery of the whole of the ammonia, including that combined with the non-volatile acids, without causing injury to the apparatus.

The fresh ammoniacal liquor runs from the tank into a boiler 7-8 metres long (23-26 feet), where it is heated; it then passes into the second boiler, heated by direct fire, thence to the third boiler, which is not in contact with the fire gases, where it is treated with lime to decompose the non-volatile ammonia compounds; finally, after exhaustion, it is run off. In regular working, the second boiler is heated; the fire gases which leave it surround the first boiler, and bring its contents to the boiling point. The vapours evolved in the second boiler pass into the third through a pipe which has a rake-shaped end; in this boiler they drive out the ammonia set free by the milk of lime, which is introduced through a funnel. The ammonia, together with steam, passes through a pipe into the preliminary heater, where it takes

¹ "Polyt. Journ.," Vol. CCXXIX, 1878; Ger. Pat. 351, of 13 July, 1877.

up the volatile ammonia compounds, and, with these, passes through pipes into covered leaden boxes, filled with 50 per cent sulphuric acid. The gases evolved here, principally sulphuretted hydrogen and carbonic acid, are taken through a flue to the fireplace of the second boiler, and so rendered harmless.

When the acid in the saturators is neutralized, the liquor obtained is allowed to cool and the crystallized salt collected on drainers, whilst the proper quantity of sulphuric acid is added to the mother liquor and the mixture again treated with ammonia vapours, so that a separate evaporation is not required.

If sal-ammoniac is to be made, the leaden boxes are replaced by stone tanks filled with hydrochloric acid; in this case evaporation of the liquid cannot be avoided.

This apparatus has already been introduced into the ammonia works at Cologne, Hamburg, Stettin, and Leipzig. It has been found easy to work, the necessary repairs are small, and the gas liquor is completely utilized.

Sal-ammoniac from Gas Liquor.—The liquor is treated¹ either by distilling with a quantity of lime, proportioned according to the quantity of ammonium chloride or sulphate to be produced, and the evolved ammonia led into hydrochloric acid, or the gas liquor is immediately neutralized by acid. The finest product, almost chemically pure, is obtained by the former process.

In this process the liquor is heated with quicklime in a capacious still to boiling, the vapours taken through a coil cooled by water, in order to condense the greater quantity of the water, and the distillate allowed to flow into a tank containing hydrochloric acid. This tank is a wooden box lined with thick sheet lead, and closed by a cover. A pipe conducts the unabsorbed gases—sulphuretted hydrogen, etc.—under the fire grate of the still, where they are burnt and from whence they pass into the chimney. The end of the

¹ Stohmann, Muspratt's "Chemie," 3rd ed., Vol. I.

coil dips into the acid, so that the ammonia, which is only partially condensed in the coil, may be entirely absorbed.

After about one-tenth of the liquid in the still has evaporated, all the ammonia appears to be driven out, a point which is recognized when a red litmus paper, held in the steam issuing from a test-cock, is no longer, or only slightly, turned blue. This tap is then opened and the still emptied, the air entering through the tap thus preventing the sal-ammoniac solution from rushing back.

The ammonia gas is allowed to pass into the acid until the latter is just neutralized, when the salt solution is drawn off and the receiver charged with fresh acid. Generally the sal-ammoniac solution is so concentrated that it requires but little evaporation in order to attain the strength requisite for crystallization. It is then allowed to cool, when a fine crop of crystals, almost white in colour and completely free from tarry matters, is obtained.

The distillation can be more conveniently conducted if two boilers are connected together by pipes and cocks in such a manner that the vapours from one can be passed into the other. The first boiler is then heated by direct fire; the latent heat of the steam brings the liquor in the second to boiling and volatilizes the greater part of the ammonia, so that the ammonia from both quantities of liquid passes in the vapours through the second boiler into the acid. As soon as the first boiler is exhausted, its contents are run off; it is then refilled and fire made under the second boiler, in order to drive steam from it into the first and the ammonia thence into the acid, until the second vessel is exhausted, when it is again filled. Great economy in fuel is thus effected, since double the quantity of ammonia can be obtained by using very little more fuel than would be required for the distillation of the liquid in one boiler. There is also the advantage that much less steam passes over with the ammonia gas, and thus a much more concentrated sal-ammoniac solution is obtained.

Quite a number of methods of recovering ammonia from

gas liquor have been patented, the usual process being perfectly automatic. The still is an upright cylindrical cast-iron vessel divided into shallow compartments communicating one with another at opposite sides. The gas liquor is pumped in at the top and flows from one compartment to another, meeting on its way a current of steam passing in the opposite direction. In the upper half of the still the free ammonia and the volatile ammonium salts are driven off. At about half the height of the still a graduated quantity of milk of lime is pumped in by a small pump at the side. This decomposes the fixed ammonia salts. The spent wash passes out at the bottom of the still. The vapours containing ammonia and volatile ammonium salts pass over by a lead pipe into a bell-shaped device suspended in a lead-lined tank containing sulphuric acid which absorbs all the ammonia, decomposing the salts. To prevent any nuisance from the sulphuretted hydrogen, etc., which is evolved, a small pipe passes from the bell into an oxide of iron purifier which absorbs the sulphuretted hydrogen. The sulphate of ammonia separates in fine crystals when the acid is saturated. It is scraped out and laid on a lead floor to drain and usually shows a greyish or bluish colour. It is in this state used directly as a fertilizer and forms one of the most concentrated sources of nitrogen in an easily available condition.

The amount of ammonia recovered from coal is now very considerable, as will be seen from the following figures taken from the Annual Report of the Chief Alkali Inspector for 1915:—

AMOUNT OF AMMONIA RECOVERED IN THE UNITED KINGDOM
(Expressed in Terms of Sulphate). Tons.

	1913.	1914.	1915.
Gasworks	173,075	175,930	182,180
Ironworks	15,142	16,008	19,956
Shaleworks	58,826	62,749	63,061
Coke ovenworks	145,406	137,430	133,816
Producer, gas, and carbonizing works (bone and coal)	33,218	34,295	33,695
Total	<u>426,267</u>	<u>426,412</u>	<u>432,618</u>

The most recent development for the recovery of ammonia from coal gas is that known as the "direct" method, in which, instead of treating the liquor condensed from the gas, the gas itself is passed through dilute sulphuric acid contained in an apparatus known as an acid "bubbler," but many difficulties have been encountered, and the process cannot yet be regarded as a perfect success in gasworks although at coke ovens it has proved to be advantageous.

In the patent granted to the Deutsche Continental Gas Gesellschaft, Dessau and K. Fritz, Darmstadt (Ger. Pat. 291,038), it is proposed to recover the combined ammonia from gas liquor by heating it with the mineral constituents of solid fuel, such as wood, peat, coal, etc., employed in the form of ash, clinker, or coke breeze in place of lime. The action of these materials is stated to be due to the action of iron oxide, magnesia, and lime in combination with silica or alumina. The gas liquor may either be run through a layer of the material, or else treated with an aqueous extract of the same, the liberated ammonia being expelled and recovered in the usual manner. The process can be made continuous by employing a number of boxes, adapted to be out of the main circulation for recharging.

Preparation of Ammonia from Guano.—In 1841 Young took out a patent for obtaining ammonia from guano.¹ Vertical cylindrical retorts are filled with two parts of guano and one part of slaked lime or any other caustic alkali. The two substances are mixed with a stirrer, then gently heated, and the temperature slowly raised to a red heat. Through the combined action of heat and the alkali, the whole of the nitrogen in the guano is converted into ammonia. Thus not only the ammonium salts already present, but also the nitrogen of the organic compounds, always present in guano, are obtained in the form of ammonia. It would not, however, be economical to use guano as a source of ammonia, since it contains phosphates which would be wasted. It is best used as a manure, as in this case both the ammonia and the phosphates are utilized.

¹ Muspratt's "Chemie," 3rd ed., 1874, Vol. I.

The Dry Distillation of Bones produces a liquid which contains a large quantity of ammonium carbonate. Taming obtained ammonia solution from this liquid by first adding calcium chloride, insoluble calcium carbonate and ammonium chloride (sal-ammoniac) being formed. The liquid was then separated from the precipitate and boiled for an hour. All the volatile and gaseous impurities were thus removed. As soon as the liquid had cooled, it was mixed with a sufficient quantity of ferric hydroxide, by which all the sulphur compounds were converted into insoluble sulphide of iron. Milk of lime was then added in order to set the ammonia free, and the liquid finally distilled.

L. l'Hôte¹ utilized the waste of wool, hides, leather, horn, feathers, and sponges, which contains 6-15 per cent of nitrogen, in order to obtain ammonium sulphate. When these waste matters are treated with a solution of caustic soda in from nine to ten times its weight of water, preferably in the cold or at a gentle heat in order to avoid loss of ammonia, some are dissolved, whilst some entirely lose coherence. The slimy liquid so obtained is mixed with slaked lime to a paste, which is brought into an iron retort, connected to receivers, in which is placed chamber sulphuric acid. The mass is then distilled at the lowest possible temperature, in order to prevent the dissociation of the ammonia; when the evolution of gas has ceased, the retorts are heated to a red heat. After the operation there is left in the retorts a white powdery residue, consisting only of sodium carbonate and quicklime. On treating this with water caustic soda is again formed, which can be used for the next operation. The ammonium sulphate obtained is coloured, but it may be purified by crystallization.

¹ "Compt. rend.," 76, p. 1085; "Dingler's Journ.," 209, 1873.

CHAPTER XXXIX.

PETROLEUM RESIDUES.

Preparation of a Resin-like Substance from the Sulphuric Acid Used in Refining Petroleum.—W. P. Jenny, of Boston, has obtained a patent for the preparation of a substance similar to resin from the waste sulphuric acid of petroleum-refining. The sulphuric acid, which has been used for refining petroleum or shale oil, is mixed with an equal volume of water, when two layers form, the upper consisting of a thick oil of objectionable odour, the lower of dilute sulphuric acid. The oil is repeatedly washed with boiling water, finally with the addition of a little soda, and is then distilled. After the oil distilling below 250° C. has passed over, a current of air is blown by means of a suitable arrangement for forty-eight hours through the residual oil, the operation being conducted in the retort used for the distillation. During this process the oxygen of the air is eagerly absorbed by the oil, which, on cooling, solidifies to a deep brown mass similar to resin.

Another method for obtaining this resin consists in heating the residual acid, which contains the oil in solution, for several days at 100-150° C., until a test portion sinks when poured into water. The mass is then poured into water and washed with a large quantity of water, or, if necessary, an equal volume of petroleum ether is first added. In the former case the resin separates on the bottom of the washing vessel; in the latter case it remains dissolved in the naphtha, and floats on the surface of the acid.

The product, which is more or less hard in its nature according to the extent of the oxidation, is insoluble in water,

calies, and alcohol, but dissolves readily in fats, animal and vegetable oils, naphtha, benzol, chloroform, ether, carbon sulphide, amyl alcohol, spirits of turpentine, and in sulphuric acid of 66° B. When melted with gutta-percha or outhouc in varying proportions, it forms an elastic substance which can be used for insulating purposes.

Tar and Other Products from Petroleum Residues.—Lefny has investigated the composition of tar obtained in making illuminating gas from petroleum residues.¹ In this method of making gas the petroleum residues are subjected to dry distillation in retorts filled with wood, when they produce illuminating gas and a tar of specific gravity 1.015. If the latter is passed through the retorts a second time, only a very small quantity of gas is produced, and the tar is but little altered; it has now a specific gravity of 1.207, and possesses all the properties of a tar. It begins to distil at 80° C., and gives fluid distillates below 200° C.; at higher temperature solid substances are formed, but later, above 300° C., oils again come over, which, however, separate crystalline compounds. A more examination of the distillate gave—below 200° C., 13.9 per cent, containing 4.6 per cent of benzene, 5.2 per cent of toluene and xylene; from 200-270° C., 26.9 per cent; from 270-340° C., 8.6 per cent, containing naphthalene, cumene, and petroleum; above 340° C., 27.5 per cent, containing 3.1 per cent of pure anthracene; the residue in the retort was 5 per cent.

This tar affords the possibility of utilizing the petroleum residues in districts which are rich in petroleum, to produce substances which can be used in the manufacture of aniline dyes and alizarine. The quantity of petroleum residues produced in Russia alone was estimated by Lefny at 98,000 tons per year 1878. Of this only a small portion was used for running the distilling apparatus, another portion went into the interior of Russia for gas-making, whilst more than half

¹ "Polyt. Journ.," 229, p. 353; Post's "Zeits. f. d. chem. Grossgew.," III, 44, 506.

remained, and was burnt up outside the works, owing to lack of storage. There is no doubt that in the future there will be found in these petroleum residues a valuable material for the production of aniline, alizarine, etc.

In order to ascertain the conditions most favourable to the formation of tar, petroleum residue of specific gravity 0·872, and boiling at 270° C., was passed through red-hot iron pipes 1·24 metres (4 ft. 1 in.) long and 5 cms. (2 ins.) wide, filled with carbon. Irregular heating gave rise to very different results. In one case 100 grms. gave 23·9 grms. of tar and 30·1 litres of gas; another experiment yielded 46·4 grms. of tar and 59 litres of gas. At higher temperatures the yield of gas was higher—up to a certain temperature, above which the yield again became less. Without carbon the decomposition in the pipes proceeded irregularly, until a carbonaceous deposit had formed by the destruction of a portion of the petroleum, which deposit then facilitated the decomposition. The action is the same when the pipe is filled with broken brick, asbestos, etc. Very porous carbon, platinized, was still better than ordinary carbon; those catalytic substances which most readily absorb gases cause the production of the most tar. If the tar produced be again passed through the pipe under pressure it is considerably decomposed, carbon being deposited. Without increase of pressure, however, it suffers practically no alteration. The specific gravity of the tar never exceeds 0·8889; it contains a mixture of amylene and benzene, 6·28 per cent; benzene, 12·56 per cent; toluene, 10·5 per cent; mixture of toluene and xylene, 6·8 per cent—in all 52·5 per cent boiling below 320° C., and 35·0 per cent above 320° C. Solid hydrocarbons, such as naphthalene and anthracene, could not be detected, which is ascribed by Letny to the fact that the petroleum vapours have passed through too short a layer of carbon. In fact, when gas retorts are used, the yield of tar is lower the less coal is present in the retorts; accordingly the quantitative yield of tar, and the percentage of solid hydrocarbons in it, is proportional to the dimensions of the layer of carbon

through which the petroleum vapour is passed. In working on the small scale, amylene, hexylene, etc., were always formed; but not when gas retorts were used. Steam passed through the retort together with the petroleum residues was without action; and, on the other hand, by the application of pressure the yield of tar was always reduced. Similarly to the tar, the gas differed in composition according as it was made on the large or small scale. In the latter case it contained, in addition to hydrogen and marsh gas, ethylene, propylene, butylene, acetylene, and crotonylene.

Petroleum Residues as Fuel for Cupola Furnaces.—The introduction of pulverized fuel in cupola furnace practice effects, on the one hand, the oxidizing action of the excess of blast, and, on the other hand, prevents the formation of protuberances on the tuyères, and the attendant inconveniences. The carbon deposited on the walls of gas retorts, and the residues obtained in petroleum refining, are the most suitable fuels to be used in the pulverized state, since they are completely free from ash. W. Batty, of New York, injects these substances, in a state of fine dust, with the blast, and obtains the following advantages: (1) The whole of the oxygen, as it enters the zone of fusion, can at once combine with carbon, by which means a powerful neutral or reducing flame is produced—the quantity of carbon introduced can readily be regulated as may be necessary; (2) the iron becomes hotter, and instead of oxidation occurring through the presence of an excess of air, the iron readily takes up carbon in the atmosphere of carbonic oxide impregnated with heated carbon; (3) in consequence of the higher temperature, the slag is more fluid; hence (4) the formation of protuberances on the tuyères is avoided; (5) the loss of metal is lower. On account of the partial carbonization of the iron, the possibility of selecting scrap-iron, which is, as far as possible, free from sulphur and phosphorus, is of especial importance to the quality of the castings.

Utilization of the By-Products and Chemicals of Mineral Oil Works.—Grotowsky has made certain noteworthy obser-

vations on this subject,¹ according to which the carbolic acid may be separated from the so-called creosote-soda, produced in refining the crude oils, either by means of the dilute sulphuric acid, also produced in refining, or by means of carbonic acid made for the purpose. In the former case Glauber's salt; in the latter soda, or, in the event of again causticizing by lime, caustic soda, are produced. The separated carbolic acid is either merely washed with water and then brought into the market to be used for disinfecting purposes and for saturating wood, or it is converted by distillation into the so-called creosote oil. The latter is then used for making phenol dyes or for disinfection. By repeated solution in caustic soda, decomposition by sulphuric acid, distillation over iron filings, and finally over green vitriol, a quite pure pale oil is obtained. The empyreumatic resin, which dissolves in the sulphuric acid during refining, is separated from the acid again by high-pressure steam. The dilute sulphuric acid then obtained may be applied in the manufacture of superphosphate, or as indicated above. The separated empyreumatic resin is washed with water and subjected to distillation either alone or together with creosote. In the distillation more or less is removed according to the purpose for which the product is intended: in the case of tar for roofing felt, only until the residue forms a stiff paste, but for asphalt, to be used as the binding medium for coal briquettes, until the mass, when cold, has a shining, brittle fracture.

Regenerating Spent Sulphuric Acid from Refining Tar Oil or Petroleum—(Ger. Pat. 291,775, C. Still, Recklinghausen).—The crude, recovered acid, whilst still warm and fluid, or after dilution to the desired degree, can be immediately regenerated to pure liquid sulphuric acid by spraying it through a nozzle with high-pressure steam or hot compressed gas. A friable solid residue is left, and all the volatile constituents, such as residual traces of oil, and the malodorous decomposition products formed during the treatment of the acid, escape with the outgoing steam or gas. For this pur-

¹ Post's "Zeits. f. d. chem. Grossgew.," III, 2, p. 345.

pose the crude acid is run into a collector, which is heated by an internal steam coil. From this vessel the fluid acid is run into a pulverizing nozzle, which is built into the wall of a closed chamber and fed with steam. The bottom of this chamber slopes down toward the opposite side, so that the liquid condensed during the process can drain away to an open pocket outside, for which it forms a seal, so that none of the gaseous contents of the chamber can escape. When this liquid reaches a certain level it is drawn off automatically into a collecting vessel. The cover of the chamber carries a flue, fitted with baffle plates to retain particles of liquid carried upward with the steam, etc., the latter being aspirated, by means of an injector nozzle, into the condenser, which discharges into a collector. The permanent gases are led from this latter into a washer charged with an alkaline washing liquor, which eliminates any injurious acid fumes, such as sulphur dioxide. The solid residue from the crude acid falls on to the sloping floor of the chamber and slides down into the pocket outside for removal.

CHAPTER XL.

BY-PRODUCTS IN THE MANUFACTURE OF ROSIN OIL.

*Recovery of Acetate of Lime from the Acetic Water of the Rosin Distillation.*¹—The acetic liquor is neutralized with lime in large wooden vessels, when acetate of lime is formed, and a brown insoluble compound of lime with resinous matters separates at the surface and is removed. The clear liquid, obtained by filtering, is evaporated to 5° B., and then a strong solution of Glauber's salt added so long as a precipitate of sulphate of lime is formed. The whole of the acetate of lime is not, however, converted into sulphate of lime, accordingly the undecomposed remainder is precipitated as carbonate of lime by means of carbonate of soda. The liquid, freed from the precipitate by filtering, and now containing only sodium acetate and a little calcium sulphate in solution, is evaporated in shallow cast-iron pans to crystallization; the resinous matters which separate during the evaporation are removed. The crystallizing point is reached at 15° B., the liquid is then drawn off into the crystallizing tubs, in which, after four days, it deposits the sodium acetate in large crystals, which are once or twice recrystallized.

The sodium acetate obtained is subsequently fused in flat cast-iron pans. It first melts in its water of crystallization, after the evaporation of which the salt again becomes solid; it is then fused a second time at a higher temperature. The mass of salt swells up, evolves oily vapours, and finally melts quietly; it is next removed from the pan, dissolved whilst still hot, and the solution filtered. The filtrate is left to crystallize, the sodium acetate decomposed by strong sulphuric acid in an iron pan lined with lead, with a copper

¹ "Die Harze und ihre Producte," G. Thenius. Vienna, Hartleben, 1895.

or lead head, and the acetic acid distilled over; it is again rectified in a glass retort with a little pyrolusite. It is then water-white, and free from foreign odour.

Preparation of Acetate of Iron from the Acetic Water of the Rosin Distillation.—The acid liquor obtained in the distillation of colophony is brought into barrels filled with small particles of iron—sheet-iron clippings, iron turnings and borings. In about eight to fourteen days the saturation of the acid is complete; it is accelerated by frequently drawing off the liquid, so that the iron in the barrels may come into contact with the atmosphere, which hastens the oxidation. The dilute acid in the barrels is also kept at a temperature of 25-31° C. by frequently injecting steam. However, the saturation is not always complete in the barrels; the solution is therefore drawn off, and heated to boiling in iron pans similarly filled with iron. The resinous matter which rises to the surface is skimmed off, and the process continued until the acid is completely saturated. The liquid is evaporated down to 10-15° B., and allowed to settle thoroughly before use. It forms a dark, blackish-green solution. Acetate of iron is extensively used in the calico-printing industry.

Utilization of Rosin Oil and the Residue of the Distillation in the Manufacture of Soot-blacks.—Rosin oil gives, when burnt in special stoves, a very fine soot, highly prized by manufacturers of lithographic and printing inks. In order to obtain the black from rosin oil, the latter is allowed to flow from a separate tank through a narrow pipe, whence it falls upon a red-hot plate contained in the stove; the oil is decomposed, the soot drawn into the depositing chambers, where it settles in various qualities. As soon as a certain quantity of oil has been burnt, and the stove, having stood for a sufficient time, is quite cold, the separate collecting chambers are opened, and the soot removed. The finest soot for lithographic purposes is always found in the furthest chamber, whilst a less fine black, used for letterpress inks, collects in the nearer chambers. The soot is graded by sieving.

The residue of the distillation, containing much rosin, is burnt in a special soot-stove; it produces lower qualities of black, which are similar in value to the soot of ordinary flames. From the burnt residues the sodium carbonate may be regained by extracting with water, filtering, and evaporating.

See also "The Distillation of Resins," by V. Schweizer (Scott, Greenwood & Son).

CHAPTER XLI.

SOAP-MAKERS' WASTE.

There is a considerable amount of waste soap cuttings produced in all soaperies. These are added to the pan in the boiling and facilitate saponification by bringing the oil and alkali into more intimate contact.

Waste-Soap Cuttings ("Neue Seifensieder-Zeitung").—Manufacturers, who possess a pan heated by steam or in a water-bath, can readily melt together and again press the cuttings of toilet soap. The soap to be melted is cut up into shavings by means of a wire or plane, and brought in small quantities at a time into a pan heated by steam or on a water-bath. The soap is there allowed to melt, with the addition of a little water, or, if the soap becomes too thick or acid, of spirit. The quantity of water to be used is determined by the condition of the soap; if it be dry more water is used than if it were wet. If water-glass has been used in softening the soap, it is necessary to add a few pounds of potassium carbonate (20-22° B. to prevent the separation of silicic acid. Carefully, care must be taken that the soap does not froth, and frothing is accomplished by stirring diligently, and adding water if required. The water is only added in order to assist the melting of the soap, but not to dissolve it. When the soap is completely melted, the colouring matter is added, and then the perfume, before pouring into the moulds. These soaps are generally coloured yellow, red, or blue, and made into household, Windsor, mottled, coal-tar, or sand and pumice soaps.

When melting the cuttings, if the soap should froth or become too thick and lumpy, and if a small addition of spirit

is without result, the following method is adopted: Whilst stirring, sufficient water is poured into the pan to dissolve the soap completely to a thin liquor; it is then salted out with a strong hot solution of salt, the salt liquor removed, and the soap brought together by potash lye of 2-3° B. or hot water. After the soap has stood for some time, it is drawn off down to the deposit at the bottom, coloured, crutched in the cold, perfumed, and poured into the mould.

The following directions for making brown Windsor soap by melting together cuttings may serve as an example of this method of treatment. For a brown soap are taken the cuttings of such coloured soaps as yellow, blue, and brown. 50 lb. of soap are coloured brown by 120 grms. (4 oz.) of caramel, and then scented with 40 grms. of oil of lavender, 30 grms. of oil of thyme, 30 grms. of cumin oil, 30 grms. of oil of cloves, and 30 grms. of cinnamon oil. The caramel is obtained by carefully melting ordinary sugar in a pan, with constant stirring, until it has changed into a mass, which runs from the stirrer in dark golden-yellow threads.

Utilization of Waste Soapy Waters.—The utilization of the waste soapy waters produced in such large quantities in public laundries and in many industries, i.e. the separation of the fatty acids which are combined with alkali in these waters, has been many times attempted, but with little success. The methods often recommended—collection of the soap-suds in tanks, decomposition of the soap, allowing to deposit, etc.¹—can only be applied to small quantities of strong soap liquors, such as are produced in wool-washing. In the case of public laundries, which use daily 150-200 kilos (3-4 cwt.) of soap in 60,000-70,000 litres (13,200-15,400 gals.) of water, the application of such methods is quite impossible. In such cases, in order to collect the suds, the waste waters should be run, together with a regular stream of lime water, through the apparatus shown in Fig. 20. A tub *A* is half-filled with slaked lime; a regulated current of water passes through the pipe *d*, the tub *A*,

¹ Heuze, "Dingl. Polyt. Journ."

and the outlet, carrying lime into the vat *B*. The water from which the soap is to be removed enters at the same time in a continuous stream and leaves at *b*. It is then only necessary to run the mud deposited on the bottom of the vessel into the filtering basket *D*, placed below, by raising the plugs *c*. The lime soap collected in the basket is decomposed with hydrochloric or sulphuric acid and steam, the cooled mass again brought into the filter basket, washed, and freed from water by draining and pressing. The fatty mass obtained is still by no means pure enough for the fat press. In the case of waters from a public laundry, it contains

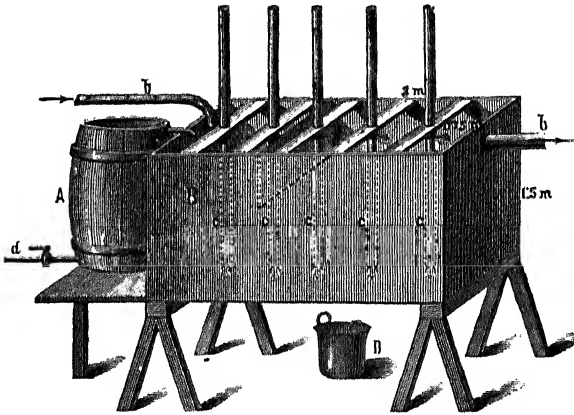


FIG. 20.

40-50 per cent of foreign matter—sand, pieces of wood, and cellulose—so that the production of fat therefrom is not a remunerative operation, apart from the cost of the apparatus. It is more economical to recover the fat by extraction with carbon bisulphide, a method already much in use. An apparatus very suitable for this purpose is shown in Fig. 21. It consists of the water-bath *A* and the boiler *B*, contained in *A*, for the reception of the fat. The impure fat is placed in *C*, *D* is the condenser, and *E* the storage vessel for the carbon bisulphide. After the cylinder *C* has been filled through *a* with fat, which lies on a perforated bottom between the opening *k* and *l*, carbon bisulphide is admitted from *E* through the

tap *i*. It dissolves the fat contained in the impure mass and carries it through *c* into the boiler *B*, in which the carbon bisulphide evaporates. The vapour rises through the pipe *b* into the condenser *D*, where it is condensed, the liquid then passing to *C*, whence it again carries fat to *B*. When all the

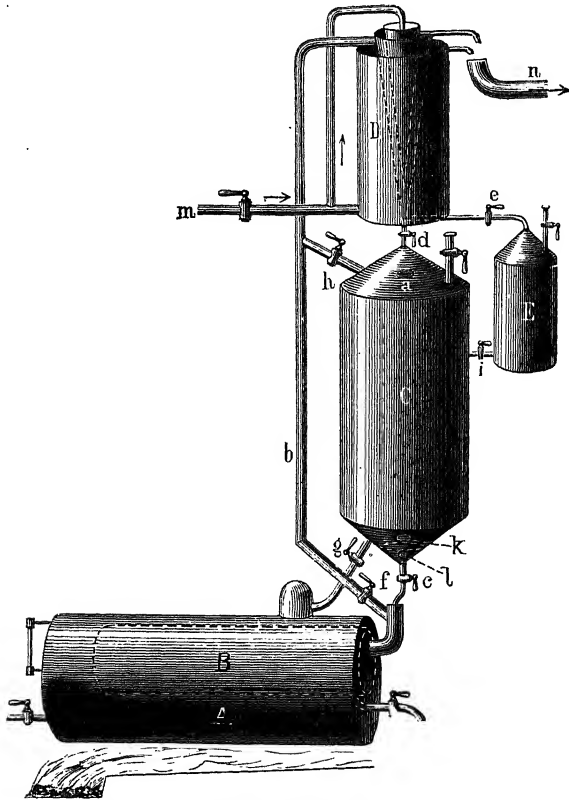


FIG. 21.

fat has been removed in this manner, the taps, *c*, *f*, *g*, and *h* are opened, whilst at the same time *e*, *d*, and *i* are closed. Steam then passes from *A* through *g* into *C*, expels through *h* the carbon bisulphide, which collects in *E*, together with that evaporated in *B*; *k* and *l* are openings for emptying the cylinder *C*. By this arrangement of the apparatus, not only

is all the fat recovered, but also the loss of carbon bisulphide is reduced to a minimum, assuming that the necessary quantity of cold water is supplied to the vessel *D* through *m*. The fat remaining in *B* still requires refining, which is accomplished in the usual manner.

Utilization of Liquids Containing Fatty Acids.—In all the textile industries there is formed a number of waste liquors containing fatty acids, the quantity of which is so considerable that its recovery is at times a source of not inconsiderable profit. In regard to the composition of these liquors, there are in general three different kinds to be distinguished: (1) The waste liquors obtained in removing the perspiration and grease from wool and woollen fabrics, to which are to be added the waste soapy waters of houses and large laundries; (2) the used soap liquors obtained in boiling silk to remove the "gum"; (3) the waste liquors of Turkey-red dyeing, which contain oil. In all the liquids mentioned the fatty acid compounds are mainly united to alkalies; accordingly their separation by a strong mineral acid appears to be suitable, and this method is almost always used when these liquids are treated. The method is, however, attended with so many inconveniences that many industrial establishments are averse to the utilization of these waste products. In the first place the liquids, in addition to the alkali compounds, always contain lime soaps produced by the lime in the water. When the oils and fats are separated by sulphuric acid, or by crude hydrochloric acid, which always contains sulphuric acid, the lime is always separated as sulphate, which forms a pasty mass with the oil. This mass is not readily separated from the water, so that its application in making soap or illuminating gas is not easy. Also, the storage of the fluid oil in barrels is laborious and subject to considerable loss. Thus the desirability of separation of the fatty acids in the form of a solid compound of fairly constant composition appears to be indicated. Vohl has previously shown¹ that, when lime or a lime salt is added to these liquids, all the fatty matter is

¹ "Muster-Zeitung," 1873.

separated as a solid lime soap, from which the liquid can readily be drawn off, and which can be stored in the dry state. This lime soap is a substance which can readily be transported and sold to works occupied with the separation of oil and fat from such material. It is, of course, not the case that each establishment carries out the complete utilization of its own soap waste, but simply that it removes the fat from its waste soap-suds with lime, and then sells the lime soaps, which contain about 40 per cent of acids, to the proper works. The apparatus required for this precipitation of lime soaps is of an extremely simple nature, and easily obtained. Since lime soaps give rise to the formation of gypsum when treated with crude hydrochloric acid, which always contains sulphuric acid, and the gypsum makes the separation of the oil from the aqueous liquid very difficult, Vohl experimented with a magnesium salt, by which the fatty acids are as completely precipitated. The magnesium soaps occupy a much smaller volume, contain about 60 per cent of fat, and produce no gypsum when decomposed by sulphuric acid, or hydrochloric acid containing sulphuric acid. The lime and magnesia soaps may also be directly employed for the manufacture of illuminating gas; the tar, which is simultaneously produced, may be used like pure oil in gas-making. The gas obtained from the lime and magnesia soaps is of very high illuminating power, and the yield is very considerable.

The Residues of Oil-manufacturing are recommended by G. F. Reisenbichler to be used in soap-making.¹ After they have been subjected to the strongest pressure, oil seeds retain 5-10 per cent of oil, which can only be extracted by chemical means. These residues may be used with great advantage in soap-making in the case of very cheap soaps; a small quantity is added, not exceeding 20 per cent. The residues from expressed nuts of all kinds are especially suitable; less suitable, or not at all, are expressed linseed and rape seed, since they contain too many hard particles. When these fatty residues are to be added to soaps, they must be fresh, and previously be

¹ "Neue Seifensieder-Zeitung."

finely ground. They are then mixed directly with the lye, which is then boiled, and later the principal fat added to the resulting thick liquor. The saponification is much accelerated by the addition of this powdered material to the lye, and the consequent thick condition of the latter. Reisenbichler recommends in particular for this purpose the residuals obtained in expressing olive oil from the olive. The cake, which contains fairly fine skins and is very oily, readily dissolves in the lye to form a tolerably uniform paste.¹ "Oil foots" are also used in soap-making.

Recovery of Glycerine as a By-product.—Glycerine is obtained by saponification of fats and as a by-product in the preparation of fatty acids. In soap-making small quantities of glycerine were formerly obtained; according to Schwanert² the liquid below the supernatant soap—the so-called under-lye—which contains glycerine, alkaline hydroxides, sodium and potassium chlorides, was exactly neutralized with hydrochloric or sulphuric acid, evaporated to dryness on the water-bath, the residue extracted with 90 per cent alcohol, and the glycerine obtained as a yellow syrup on evaporation of the extract in a still. According to Reynolds, the under-lye was concentrated by evaporation, the salt deposited on the bottom of the pan was removed from time to time and brought into a drainer, from which the liquid could flow back into the pan. When the liquid had reached such a concentration that it boiled at 109° C., it was heated in a still until its boiling point rose to 193° C., when high-pressure or superheated steam was driven through the upper layers of the liquid and the glycerine distilled over in the steam. It was necessary to regulate the temperature carefully, so that the glycerine should not be decomposed at too high a temperature, and that the distillation should not be stopped by too low a temperature. After the distillation, the distillate was evaporated at a moderate

¹ Elsner regards these additions as not permissible, and soap made in this manner as adulterated.

² Muspratt's "Chemie".

heat, when the glycerine remained behind. When this method of manufacture is considered, it can readily be understood that glycerine can now be made very cheaply and on a very large scale from the under-lyes of the soap-maker, also it can be regained, readily and cheaply, from the crude glycerine obtained in the manufacture of stearin candles. But although small soap-works may not be able to work up the under-lyes for glycerine in this manner, experiments in other directions must not be omitted. Linke first drew attention to the large quantity of glycerine lost in these lyes, which he estimated at 8,500,000 kilos (8500 tons) per annum in Germany alone, of a value of 3,000,000-3,600,000 marks (£150,000-£180,000). These figures explain the attempts which have been made to find a method by which glycerine can be recovered from this liquid, and Schwanert made a step in the right direction when he drew attention to the crystallizability of glycerine, by means of which property it may perhaps be recovered more profitably from soap-lyes. In 1867, Sarg had already obtained crystalline glycerine at several degrees below zero, but Kraut, of Hanover, was the first, in 1870, to discover a method of crystallizing glycerine in any required quantity and quality. The method was transferred to Sarg, Son and Co., of Liesing, near Vienna, with all right of priority. This firm obtained patents in Austria, England, and Russia, and worked the process on the large scale. The crystallization is conducted in sheet-iron vessels from which the crystals can readily be loosened; they are then freed from the adherent mother liquor by treatment for fifteen minutes in a centrifugal running at 1200 revolutions per minute, and after they have dried are melted. Crude glycerine must be once recrystallized. As Schwanert states in these communications, the temperature has a considerable influence on the yield; at temperatures higher than 2° C. the mother liquor amounts to more than 30 per cent of the glycerine used. In mild winters the crystallization is not profitable. In addition to the application of a temperature several degrees below zero, a certain amount of movement

appears to be one of the conditions under which the glycerine becomes solid and crystalline. Experiments with a view to crystallizing glycerine in a simple manner, applicable to larger quantities, would certainly be very profitable, since the most complete purification is obtained in this manner, all the impurities remaining in the mother liquor. The under-lyes of soap-works might by this means be utilized in a most productive manner.

A process for the *recovery of glycerine from waste soap-lyes*, due to H. van Ruymbecke, consists in new means for evaporating, distilling, and concentrating these lyes. The apparatus is constituted of cylindrical cast-iron evaporators with the usual accessories—steam-pipes, man-holes, valves, etc.—to which are connected two cylinders, and finally the condenser. The process is as follows: The soap lye is brought into the evaporator, mixed with green vitriol or another suitable metallic salt. Then a low vacuum, about 26 inches, is produced, and steam passed into the cylinder inside the evaporator; a concentration of 28° B. at the outflow, or 30° B. at 15° C., is then obtained. The evaporation causes the salts to crystallize out, they collect at the bottom, and may be removed, dried, and purified. At the density given above the liquid contains about 50 per cent of glycerine, while most of the salts have crystallized out. The liquid now passes into a second evaporator, where it is concentrated down to 34° B. at 15° C. Salts again separate, and are removed and dried. The evaporation is effected in two stages, because the salt impregnated with strong crude glycerine would be difficult to dry and free from the mother liquor; from the second evaporator the liquid passes into the distilling apparatus, which works under a vacuum, and in which it is heated almost to boiling by means of steam. Ruymbecke uses again expanded steam, which, injected into the vacuum of about 28 ins., induces rapid distillation. The least volatile distillate collects in the first cylinder, and is very pure glycerine; the greater part of the glycerine is found in the second cylinder; the most volatile distillate, which con-

tains much water, passes into the condenser. If the product is not sufficiently pure it is distilled again.

The method given by H. Flemming, of Kalk, for the recovery of pure glycerine from soap-lyes, depends on the application of dialysis (German patent, 12,209). Glycerine is a substance which, when in aqueous solution, does not readily pass through parchment paper, whilst the salts contained in the under-lyes can readily penetrate. In order to separate the glycerine from the salts, Flemming employs an apparatus very similar in construction to the diffuser used in sugar-works. The lyes, previously evaporated until much salt separates, flow through vessels, one side of which is made of parchment paper; water flows on the other side of the parchment paper. The process which occurs is an ordinary osmosis; the salts in the glycerine solution pass through the permeable division—the parchment paper—and dissolve in the water, a corresponding quantity of which passes through to the glycerine and dilutes it.

In working with under-lyes, which are strongly alkaline, it is advisable to neutralize with sulphuric acid before dialysing, since the sulphate diffuses more rapidly than the compounds of alkaline reaction. When the under-lye is subjected to the osmotic action for a sufficient length of time, the glycerine solution is obtained very pure, when it can be converted into pure glycerine by concentration, at first in open pans, then by distillation in a vacuum apparatus. The low cost of providing an apparatus suitable to the dialysis of under-lyes, which would consist essentially of a vessel containing frames stretched over with parchment paper, makes Flemming's process available even for small works, which can then utilize very well the under-lyes which would otherwise be wasted, and dispose of the dialysed solutions to glycerine works for further treatment.

See also "Soaps," by G. H. Hurst; and "The Handbook of Soap Manufacture," by Simmons and Appleton (Scott, Greenwood & Son).

CHAPTER XLIII.

ALKALI WASTE AND THE RECOVERY OF SODA.

Utilization of Alkali Waste. Since almost all Leblanc soda-works make sulphur from alkali waste, there remains a residue consisting chiefly of carbonate, sulphate, and sulphide of lime. According to M. Schaffner¹ this residue, from which railway embankments can be made, is especially suitable for the upper layers, where it is used instead of, or together with, river sand. The sleepers lie dry, since the desulphurized residues are porous; the latter also appear to have a considerable preservative action on the sleepers.

Schott proposed to use alkali waste in glass-making, since the sodium sulphide would serve as a reducing agent in place of coal, and lime would also be introduced into the mixture. On this point, however, Lunge remarks:² "Alkali waste always contains, in addition to calcium sulphide, excess of lime both as carbonate and caustic lime, and excess of coal, and would thus be the more suitable for the use proposed by Schott if it did not contain, with these useful constituents, certain harmful substances—alumina, ferric oxide, gypsum, etc." These constituents prevent the use of alkali waste except for the lowest qualities of glass; and, in fact, Lunge himself disposed of alkali waste to makers of beer bottles. The desulphurized residue, treated by the process of Schaffner or Mond, which is never free from undecomposed sodium sulphide, is suitable for the same purpose.

Recovering Sulphur from Alkali Waste.—The Chance process of recovering sulphur from alkali waste is one of the finest examples of the application of technical knowledge in

¹ "Dingler's Journ.," 189, p. 243.

² *Ibid.*, 216, 375.

existence. The waste, which has accumulated for years in enormous quantities in the vicinity of chemical works, is treated with water in a series of closed cylinders through which is pumped carbonic acid under pressure. The carbonic acid is generated in a lime kiln from lime or magnesite which are both used in the works. The sulphuretted hydrogen liberated from the cylinders is taken to a Claus kiln where it is burnt in a limited supply of air which combines only with the hydrogen, the liberated sulphur passing on into a chamber where part of it is deposited in the form of flowers, the remainder fusing in the bottom of the chamber and being tapped out from time to time into cylindrical moulds in the form of roll sulphur or brimstone. The operations are continuous; as one cylinder becomes free of sulphuretted hydrogen it is disconnected from the series, emptied, and filled again with the mixture of waste and water.

Utilization of the Residue of the Caustic Alkali Manufacture.—The caustic soda liquor (and caustic potash similarly) is made from 10 parts of calcined soda, 100 parts of water, and 20 parts of fresh-slaked lime, by dissolving the soda by boiling, and then gradually adding the powdered and sieved lime. The boiling is continued until there is no more sodium carbonate in the solution, the carbonic acid having united with the lime to form carbonate of lime, whilst caustic soda remains in solution. After cooling, the clear liquor is carefully drawn off and brought into closed bottles or carboys, so that it may not absorb carbonic acid from the air. The paste remaining in the boiler is then brought on to linen strainers, previously moistened with water, where the caustic liquor drains off, leaving behind the carbonate of lime. As a rule, the residue in the strainer is washed with warm water, when a somewhat weak caustic liquor is obtained, which is added in a fresh operation, i.e. when fresh caustic liquor is boiled. The washed paste is then brought into wooden boxes, which are perforated at the bottom with very fine holes, over which coarse linen is laid. Here more liquor drains away. The stiff mass is pressed in moulds

similar to those used in brickmaking. The bricks are dried on boards in the air; the dried bricks are then very finely ground and sieved in order to remove all impurities. The fine powder may then be used in various manufactures.¹

In the preparation of an artificial chalk, for which some binding medium is requisite, the mass is made plastic with an addition of water-glass as binding agent, then pressed and slowly dried. The mass thus becomes as hard and firm as natural chalk; it can easily be cut up for use as writing chalk.

For the manufacture of a fertilizer for grass: the dried residue always contains a few per cent of alkali, which cannot readily be removed by washing. In combination with other fertilizers this is very useful, especially when it is mixed with sieved wood ashes, bone meal, ground excrement, or dried blood in certain proportions. The following are very good proportions:—

Fifty parts of the ground alkali residue, 25 parts sieved wood ashes, 20 parts bone meal, 20 parts excrement, 10 parts dried blood.

Another composition: 50 parts ground alkali residue, 50 parts bone meal, 30 parts ground excrement, 30 parts sieved wood ashes.

And another: 60 parts ground alkali residue, 60 parts sieved wood ashes, 30 parts ground kainite, 40 parts ground excrement.

These are all well mixed, sieved, and packed into casks, which must be well closed.

Utilization of the alkali residue in making polishing powder and paste. The following recipes are given:—

Polishing powder: Finely powdered residue (containing soda), 50 parts; finely powdered rouge, 20 parts; finely powdered magnesia, 10 parts; finely powdered glass, 20 parts. These substances are very thoroughly ground together and the mixture sieved.

Polishing paste: Finely powdered residue (containing

¹ "Neueste Erfindungen und Erfahrungen," 1896.

soda), 60 parts; kieselguhr, well sieved, 40 parts; rouge, 20 parts; glass, finely powdered, 20 parts; magnesia, 10 parts. These substances are well mixed, and then well ground with oleine to a paste in a paint mill.

Recovery of Soda in Cellulose Works.—In regard to the recovery of soda in cellulose works, M. Faudel remarks in a long paper,¹ in the first place, that, generally speaking, in the best works the recovered soda amounts to little more than 70 per cent of the quantity used. Although the lime mud obtained in causticizing the soda be repeatedly washed with fresh water and the dilute liquors obtained be used in preparing strong liquors, and although the most rational apparatus be used for washing the boiled wood, yet there is lost in the lime mud about 5 per cent, and in the wood about an equal quantity, by leakages and in the evaporating furnaces about 20 per cent; thus, on the whole, about 30 per cent, and in some works, no doubt, much more is lost.

Faudel ascribes a portion of this loss to be due to the evaporating furnaces, which, in some works, are long, low flues with a powerful and wasteful fireplace at one end, from which the fire gases pass over the lyes. The liquors are evaporated in these furnaces only to a certain concentration; they are then removed in the form of a tolerably solid but tarry mass, and further heated and melted on separate hearths or on iron plates in the open. The soda is thus obtained in the form of large hard lumps, which frequently have to be broken and ground, at no inconsiderable cost, before they can again be used in the preparation of the lye. Quite apart from the complexity of the process, an enormous amount of heat is lost, owing to the formation of a solid crust over the surface of the lye in the furnace, which, unless broken up at the proper time, hinders the further evaporation of the liquor beneath.

According to Faudel, Porion's evaporating furnace is more rational than the one just described; the soda produced is porous, and it may be used in the preparation of fresh

¹ "Dingler's Journ.," 219, p. 432.

caustic lye without pulverizing. A furnace as used in South Germany permits the liquor to flow down a series of pans arranged in steps, so that it meets the fire gases on its way. This furnace, which is said to require frequent repairs, produces the soda in as convenient a condition as that first described, and probably, therefore, offers little advantage over it.

A fourth furnace, which appears to the author worthy of notice, is that patented by the Belgian Werotte, and known under the name of Fernau.

M. Montagnon, a Paris chemist, has proposed a method for the recovery of soda in the wet way¹ which simply consists in removing from the black liquors (of cellulose works) the gummy, albuminous and mineral matters derived from the plants. This can only be done when they are precipitated as compounds insoluble in a combination of the liberated soda with the precipitant. The compound of soda and the precipitant remaining in solution must then be treated with a base which expels the acids combined with the soda, liberating the soda which is left dissolved in the water used at the first solution. These conditions are fulfilled by certain common and cheap materials—pyrites and lime, or powdered iron ore (ferric oxide) and sulphuric acid. The cost of recovery of 1 ton of soda is given below for two methods of procedure, in which either (1) pyrites and lime, or (2) ferric oxide and sulphuric acid are used.

The cost of the recovery of soda in the wet way should not be charged entirely to its recovery, since certain by-products in great demand are also produced. These by-products may be used with advantage for bleaching paper-pulp, or may be converted into the original materials which may be again used.

In using pyrites and lime to recover the 1 ton of soda contained in 15,400 gals. of black liquor, 2 tons of calcium sulphite are formed, from which the sulphurous acid may be obtained by treatment with sulphuric acid and this can be used for bleaching paper-pulp.

¹ "Journ. des Fabricants de Papier."

When ferric oxide and sulphuric acid are used to recover 1 ton of soda, $2\frac{1}{2}$ tons of ferric sulphate are produced, which can either be sold as such or decomposed in reverberatory furnaces into ferric oxide and sulphuric acid, which may again be used in the recovery of soda.

In both cases there results about six tons of the extracted gummy, albuminous, and mineral matters, the mixture of which is sold as a fertilizer at a value of ten shillings per ton.

The following calculations of the costs make clear the relative advantages of the two processes of recovery:—

1. RECOVERY IN THE DRY WAY (PORION'S PROCESS).

	s. d.
3.7 tons of coal at 22s. 6d., for the evaporation of 70 tons of water	82 8
1 ton of lime for causticizing	20 0
Loss of soda, 20 per cent from 1 ton, i.e. 4 cwt., at 28s.	112 0
Depreciation and interest for the furnace, i.e. 15 per cent on £1600, for a daily recovery of 1 ton for 360 days per annum	13 4
Total	<u>227 7</u>

2. RECOVERY IN THE WET WAY (MONTAGNON'S FIRST PROCESS).

1.25 ton of pyrites at 24s.	30 0
1 ton of lime	20 0
Wages and general expenses	40 0
4 cwt. coal at 24s.	4 10
Loss of soda, at a high estimate, 20 per cent from 1000 kilos, i.e. 4 cwt., at 28s.	112 0
Depreciation and interest, 15 per cent of the cost of the installation, £200, i.e. per day	1 8
Total	<u>218 6</u>

Value of by-products to be deducted—	s. d.
6 tons fertilizer at 10s.	60 0
2 tons calcium sulphite at 32s.	64 0
	<u>124 0</u>
Cost of recovery per ton	<u>94 6</u>

(MONTAGNON'S SECOND PROCESS)

	s. d.
1.13 ton of ferric oxide at 20s. per ton	22 7
1.58 ton of sulphuric acid at 4s. per cwt.	126 5
Wages and general expenses	40 0
Loss of soda, at a high estimate	112 0
Depreciation and interest	1 8
Total	302 8
Value of by-products to be deducted— s. d.	
6 tons of fertilizer at 10s.	60 0
2.5 tons of ferric sulphate at 56s.	140 0
	200 0
Cost of recovery per ton	102 8

The economy resulting from Montagnon's processes over the recovery in the dry way is, therefore, for one ton of recovered soda :

First process 227s. 7d. = 94s. 6d. = 13s. 1d.
 Second process 227s. 7d. = 102s. 8d. = 124s. 11d.

Thus for every cwt. of straw treated there is a saving of eight shillings, or two shillings on one cwt. of white paper-pulp.

Recently R. Schneider has constructed an evaporating and calcining furnace for the recovery of soda in cellulose works, which appears worthy of special mention. The waste liquors of cellulose works are evaporated and the residue calcined without the production of noxious odours, by the application of highly heated air. In 1875 Siemens described a regenerative hot-air apparatus, consisting of two chambers, built of fireproof bricks, with the requisite openings for air to enter and leave, and filled with fireproof bricks after the manner of the well-known Siemens' regenerators. In Schneider's apparatus two of these chambers are connected with the calcining and evaporating furnaces. The larger stands in front of the furnace, which is somewhat smaller, about 17 metres (56 ft.) long, at a distance of about one-third of the length of the furnace from the principal apparatus. The gas obtained from lignite in the producer—a simple vertical furnace—passes through flues provided with dampers into the

hot-air apparatus, where it burns, the resulting products of combustion being then conducted, not to the calcining furnace but by flues direct to the chimney. By the proper change in the dampers a current of highly heated air from the larger apparatus enters the furnace at the end, and a second current from the second hot-air apparatus enters, in a direction at right angles to the first, the calcining space just in front of the fire-bridge. The gases pass under the wrought-iron evaporating pan, then between this and a second evaporating pan, and finally under a preliminary heater, from which they pass to the chimney, 35 metres (115 ft.) high. The liquor collected in the preliminary heater passes in the opposite direction through a pipe into one evaporating pan, thence to the second, and finally to the calcining furnace. The calcining space has a capacity of about 2.7 cub. metres (95 cub. ft.) of liquor, one evaporating pan a capacity of 7.5 cub. metres (265 cub. ft.), the other 17 cub. metres (600 cub. ft.), and the preliminary heater 29 cub. metres (1023 cub. ft.).

If we assume that the hot-air apparatus is in the prescribed condition and is supplying a continuous current of highly heated air to the calcining space, then the process is conducted as follows: The evaporating pans and preliminary heater being full, the valves are opened, the calcining space slowly filled, and the two evaporating pans again filled according to the indications of the gauge glasses. According to the consistency of the liquor, this process is repeated two or three times within three to five hours, during which time heating gases enter from the larger apparatus, in consequence of which the temperature in the calcining space rises considerably, despite the strong evaporation. When the evaporation has proceeded to a certain extent, after about three hours the current of gas is cut off, and there now enters into the larger apparatus, as during the whole period already from the smaller hot-air apparatus, only atmospheric air at a high temperature (about 1000° C.). This air is thus present in the required quantity from the commencement of the calcination and is completely

diffused through the whole of the calcining space. It would therefore appear to be impossible for any gas of organic origin to leave the calcining space undecomposed.

When the mass in the calcining furnace is completely burnt, it is drawn out through doors, and, after removing the iron plates, brought into the cooling-room. The gases which are still produced here during the slow cooling enter the calcining space through openings provided for the purpose, and burn there completely in the hot current of air coming from the larger hot-air apparatus.

CHAPTER XLIII.

RECOVERY OF POTASH SALTS.

In the patent granted to O. Delion, Cassel (Ger. Pat. 284,936), claim is made for the recovery of potash from the waste salt ("Abraum") from potash mining by treating with a solution of common salt, which extracts potassium chloride and hardens the other components of the mass, forming a product of the nature of magnesia cement.

In the past a considerable quantity of potash was obtained by the incineration of waste molasses, but these are now too valuable to be treated in this way. The residual beetroot has also been employed for the purpose, but this was found to be a mistake, since it should be fed to cattle and thus returned to the land in the form of manure.

In Russia, sunflowers are cultivated on account of their seeds, which are employed both for food purposes and for the extraction of oil. The residual stalks, etc., are then burnt to an ash which is extracted with water. On evaporation of the solution impure carbonate of potash is obtained. This can be converted into pearl-ash by treating with water, filtering, and re-evaporation. In Southern Russia this has now become a flourishing industry, there being 24 factories which in 1907 turned out 14,500 tons of potash.

Potash can also be obtained from "kelp," i.e. the ash obtained by burning seaweeds in heaps. Iodine and bromine are also obtained from the same material. The disadvantage with this material is its high content of water, i.e. about 85 per cent. It may, however, first be dried by spreading out on the sands above high water-mark. Seaweeds yield, according to Balch,¹ 500 lb. of potash and 3 lb. of iodine.

A valuable source of potash is the "suint" or sweat from

¹ C. G. Cresswell, "Journ. Soc. Chem. Indt.," 1915, 387.

the wool of the sheep. In the ordinary method of washing this is carried into the drains and finally into the nearest stream or river, but at Field Head Mills, Bradford, the dirty, raw wool, containing 40-50 per cent of dirt, and about 4 per cent of potash, is washed with soap and water. The suds are treated by the Smith-Leach process, which separates the emulsified wool grease by centrifugal action. The liquids are then evaporated and the potash extracted from the residue. According to Professor Gardner, 100 lb. of raw wool yield 18-20 lb. of grease, and would also yield 5-6 lb. of potash if this were extracted. At one time several works successfully treated this material for recovery of potash, but owing to changes in conditions of trade it does not now pay. According to Bott, 1000 lb. of wool will yield 90 lb. of potassium carbonate and 5-6 lb. of other potassium compounds. In one district in France the amount of wool washed in a year amounted, according to Bott, to 30,000,000 kilos; from this could be obtained 1,200,000 kilos of potash, of the value of £85,000. The total French production in 1890 was 4,000,000 kilos, the production showing a distinct decline.

Fertilizer from the Waste Liquor from Potash Works.—The Kaliwerke Grossherzog von Sachsen, A. G. Dietlas and K. Hepke, Dorndorf, have obtained a patent (Ger. Pat. 292,209, Jan. 29, 1915) for the utilization of the waste liquors of potash works. These liquors contain principally magnesium chloride, which on passing in gaseous ammonia is converted into ammonium chloride and magnesia, the former being suitable for use as a fertilizer, while the latter may be again converted into chloride by addition of hydrochloric acid.

CHAPTER XLIV.

SULPHUR.

Recovery of Sulphur from Sodium Sulphide.—At Stolberg, near Aix, the sulphur dioxide obtained by roasting zinc blende, etc., is cooled, and then absorbed by sodium sulphide, under the action of steam, when sodium thiosulphate and sulphur are formed, which are removed in barrels, whilst the furnace gases, freed from sulphur dioxide, pass up the chimney. From the mixture of sodium thiosulphate and sulphur the latter is distilled off, the soluble matter—sodium sulphide and sulphate—extracted from the residue, the Glauber's salt separated by crystallization from the sodium sulphide, and the former again converted by ignition with coal into sodium sulphide, which may again be used to absorb sulphur dioxide.

Sulphur from Coal Gas.—In purifying coal gas by means of Laming's mixture, there is obtained a product containing as much as 40 per cent of free sulphur, from which sulphur can be obtained by distillation over an open fire, or with superheated steam, or by extraction with heavy tar oils or carbon bisulphide.

Sulphur from Gypsum, Barytes, Alkaline Sulphates, and Barium Sulphide.—The author of the article "Sulphur" in Muspratt's "Chemistry" remarks that these methods, in spite of the cheap raw materials, have not yet attained to economic results, on account of the difficulty of separating the sulphur. Sulphuric acid has also become so cheap since its production on the large scale in smelting works, that it is used with advantage in making artificial gypsum for paper-works. (Also compare the process of Schaffner and Helbig, under "Recovery of Sulphur from Alkali Waste," p. 254.)

Sulphur Obtained in the Manufacture of Iodine from Seaweed.—In making iodine in Scotland, France, and the Orkney Islands, from kelp, the so-called vegetable sulphur separates from the mother liquors in large quantities, owing to the decompositions which take place.

Sulphur from Calcium or Potassium Sulphide is obtained as a precipitate (milk of sulphur) on decomposition by an acid (hydrochloric).

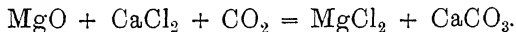
According to an English patent, J. Hollway, of London, obtains sulphur from pyrites, by passing steam over the pyrites at a dark red heat. About half the sulphur then distils over uncombined; the remainder is evolved as sulphuretted hydrogen; leaving a residue of ferric oxide.

Recovery of Sulphur from Alkali Waste.—Among the numerous methods for the recovery of sulphur, the majority of which can have no long existence since they have not succeeded in practice, the process of M. Schaffner and W. Helbig, of Aussig, which has been found practically successful, is to be regarded as especially good. These two chemists have succeeded in solving a long-attacked problem, by again making useful the plague of soda-works—alkali waste from black ash. Whilst by the processes hitherto used, which depend on the oxidation of the calcium sulphide, only half the sulphur has been regained, while all the lime, together with the other half of the sulphur, has remained as a second waste product, Schaffner and Helbig recover all the lime and all the sulphur in a usable form. Their process, as patented in Germany, for the preparation of sulphur from soda residues, gypsum, barytes, and sulphuric acid, with the simultaneous recovery, as carbonates, of the earths united with the sulphur, is based, in the first place, on the use of magnesium chloride to decompose the calcium sulphide, a reaction not hitherto applied on the large scale. The reaction is—

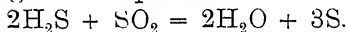


The calcium carbonate is not attacked by the magnesium chloride.

The magnesium chloride employed is obtained by subjecting to the action of carbon dioxide the residue, consisting of magnesia, calcium chloride, and the remaining unattacked constituents of the waste black ash, which remains from the action of magnesium chloride on calcium sulphide after the sulphuretted hydrogen has been driven off. Calcium carbonate and magnesium chloride are obtained according to the equation—



Instead of magnesium chloride alone, hydrochloric acid, to replace a portion, may be run in simultaneously or alternately. The acid at once dissolves the separated magnesia, when it can again exert its action. The sulphuretted hydrogen is converted into sulphur by means of sulphur dioxide, according to the equation—



However, not only sulphur and water are formed here, but also other compounds, such as tetrathionic acid—the inventors say pentathionic acid, which, according to the researches of Spring,¹ does not exist; this reaction would not be applicable on the large scale if the inventors had not found a means of preventing the formation of tetrathionic acid, etc., or of precipitating the sulphur from it if formed. This means consists in the use of a solution of calcium or magnesium chloride, in which the sulphuretted hydrogen and sulphur dioxide decompose one another. The theoretical quantity of sulphur is separated. If an excess of one gas or another be present, it is without influence on the decomposition, and is found unaltered in the solution. The function of these chlorides in the reaction is not yet ascertained; it has, however, been found that about one equivalent of calcium or magnesium chloride is required to the total sulphur present. Schaffner and Helbig have later discovered that the calcium and magnesium chlorides used in the main patent to prevent the formation of pentathionic acid, etc., in the conversion of sulphuretted hydrogen into sulphur by means of

¹ Post's "Zeits. f. d. chem. Grossgew."

sulphur dioxide, may be replaced with equal success by hydrochloric acid, sodium sulphate, magnesium sulphate, barium chloride, and sodium chloride. About one equivalent of either of these salts is used to the total sulphur present.

The alkali waste is decomposed hot by magnesium chloride in large closed iron tanks provided with stirrers. Either the black-ash waste is gradually introduced into the total quantity of magnesium chloride required to fill the tank, or the magnesium chloride solution is run on to the total quantity of black-ash waste, or finally, the two are simultaneously and slowly introduced in equivalent quantities. Loss of sulphuretted hydrogen is avoided by preventing the accumulation of pressure in the tanks and decomposers, which is easily effected by flues, fans, or pumps introduced at suitable points. In the sulphuretted hydrogen decomposers there is also always maintained a larger quantity of sulphurous acid than is equivalent to the sulphuretted hydrogen coming from the developing tanks.

The siliceous and clayey matters (clinker) present in the black-ash waste, which, if it remained in the regenerated lime, would soon accumulate to such an extent as to make it useless for soda-making, are removed by a process of stirring with water and allowing to settle, or by passing the decomposed residue through a fine sieve. The regeneration of the magnesium chloride and the lime from the decomposed residue freed from clinker is effected by the introduction of air containing carbon dioxide (flue gases, etc.).

The sulphuretted hydrogen coming from the tanks is mixed by means of mechanical contrivances in vats or towers with sulphurous acid and an aqueous solution of magnesium or calcium chloride. In the case of towers, the arrangement should be such that the sulphuretted hydrogen is introduced at the bottom and the sulphurous acid a little higher. The sulphurous acid required may be made from sulphide ores, sulphur, or sulphuretted hydrogen, or any furnace gases containing sulphur dioxide are taken and either conveyed direct to the decomposing apparatus or separately into a condenser,

similar to those used for hydrochloric acid, where they produce a solution of sulphurous acid in water, or in a solution of calcium or magnesium chloride.

This process may be applied as well to the black-ash waste as to gypsum and barytes after their previous reduction to calcium or barium sulphide. It may also be employed for utilizing and removing the injurious sulphur dioxide produced in so many metallurgical processes.

To complete the account of this process, we add a private communication made by Schaffner to Dr. Post, the editor of the "Zeitschrift für das chemische Grossgewerbe," according to which a little burnt dolomite—a double compound of magnesium and calcium carbonates—is added during the carbonation; this addition also yields magnesium chloride, which compensates for the unavoidable loss of this compound in working, amounting to 5-6 per cent. The treatment with carbonic acid, which has hitherto taken place in an apparatus similar to Weldon's manganese mud-oxidation tower by means of a powerful blowing machine, is now more economically effected in an ordinary tower with currents of gas and liquid in opposite directions.

The position of this process in practice is best shown by an article on the subject in Post's "Zeitschrift für das chemische Grossgewerbe". In answer to a question, whether the process of P. W. Hofmann for the regeneration of sulphur was applied anywhere except by Dieuze, Dr. Grüneberg stated that the precipitation was made by Mond's method and the fusion after Schaffner's method. Post states that the sulphur is now precipitated by Mond's method even in the works at Aussig, since Schaffner's precipitation apparatus, though working perfectly well, required too much labour and attention when working on an extensive scale. The oxidation of the waste is always effected by Schaffner's process, i.e. at first in heaps in the air, then by blowing in flue gases. (Mond blows air from a fan through the waste, adds an excess of the liquor to hydrochloric acid, then neutralizes by hydrochloric acid, again adds sulphur liquor, and so continues until the

vessel is full.) K. Kraushaar has described in the "Polyt. Journ." a process used with great success for many years in the works at Thann for recovering the sulphur in open vessels from alkali waste. According to Kraushaar's experiments, there forms in the interior of heaps, as far as possible protected from the entry of air, calcium hydrosulphide and hydroxide, water being absorbed. Calcium hyposulphite is not formed until oxidation occurs through air entering on breaking up the heaps, polysulphides being first formed, then hyposulphite. If now the loosened alkali waste be exposed to the air for just the proper length of time—determined by the examination of samples—that the liquors may contain to one molecule of calcium hyposulphite one molecule of calcium hydrosulphide and two molecules of calcium sulphide, CaS , then there is no evolution of sulphuretted hydrogen on the addition of hydrochloric acid, and consequently the decomposition may be performed in open vessels. At Thann the process is continuous; acid liquor in the proper proportions enters, near the bottom, a wooden vessel provided with a stirrer and heated by steam, whilst the decomposed liquor and the separated sulphur flow away continuously through a pipe near the upper edge of the tub. Kraushaar states that the process of forming the hydrosulphide is more rapidly effected than by stirring the heaps, by treating it with water and steam at five atmospheres pressure in sheet-iron cylinders; 90 per cent of the sulphur in the waste can be recovered in this manner. The remainder is then made available by atmospheric oxidation. Kraushaar suggests the use of calcium hydrosulphide liquor for unhairing hides in tanning.

This process, Post remarks, was not found successful in small experiments in the works; 90 per cent of the sulphur was not obtained. The calcium hydrosulphide appears to decompose again at the temperature employed, since on opening the apparatus streams of sulphuretted hydrogen are evolved. Since Kraushaar's process is much more costly than that generally employed, it could only count on adoption if it could recover considerably more sulphur than that hitherto obtained.

Mactear's Utilization of the Yellow Liquor from Alkali Waste.—According to Lunge,¹ Mactear manufactured at Glasgow 1500 tons of sulphur per annum from the enormous heaps of lixivated black ash, and which had given rise to great complaint. The essential part of the process is the treatment of the liquor with an aqueous solution of sulphurous acid, either with or (better) without the addition of lime. Streams of the yellow liquor, of aqueous sulphurous acid, and of hydrochloric acid are allowed to run simultaneously into the precipitating vat, the volumes of the three solutions being so regulated that as little gas and as much sulphur as possible may be produced, just as Mond has described.

A temperature of 70° C. is the most favourable for the reaction. The lixivated black ash can also find a further application in being used in place of lime in the preparation of calcium pentasulphide. If the waste be boiled with sulphur, the calcium sulphide takes up more sulphur, and a solution is obtained which contains little hyposulphite.

¹ "Polyt. Journ."

CHAPTER XLV.

SALT WASTE.

Treatment of the Stassfurt Waste Salts.—Whilst referring to one of the best and most comprehensive publications,¹ we shall follow in general the description of S. Pick² in regard to the treatment of carnallite, and draw therefrom certain further conclusions.

Carnallite is treated by a process which involves the separation of its constituents by crystallization. From the crude salt a concentrated solution of potassium chloride is prepared by the introduction of steam. The solution then comes into clearing basins, from which it flows to the crystallizing vessels. The residue is again boiled with water, and the resulting weak solution used in the next operation in place of water. The extracted residue is calcined, and its proportion of potassium chloride increased to 15-18 per cent by the addition of potassium chloride or other waste matters containing potash, when it is finely ground and brought into the market as a fertilizer under the name of "prepared kainite". The residue is also dissolved and exposed to the frost, when Glauber's salt is obtained, or it is used in the preparation of kieserite, by treating with a stream of cold water, which dissolves the smaller lumps of rock salt, leaving the larger, and carrying the kieserite away. A channel leads the water on to a sieve, where only the fine kieserite penetrates, whilst the larger pieces of foreign matter remain behind. As soon as the kieserite has collected in the settling

¹ "Die Industrie von Stassfurt und Leopoldshall und die dortigen Bergwerke in chemisch technischer und mineralogischer Hinsicht betrachtet," by G. Krause (Cöthen).

² "Die Alkalien," 2nd ed., Vienna, Hartleben.

tanks, it is shovelled out into moulds, in which it soon takes up water and sets to solid blocks.

The hot, strong solution of carnallite, after settling, is allowed to cool to 60-70° C. before the real crystallization, when a large part of the sodium chloride crystallizes out with a small quantity of potassium chloride. Or the solution is at once brought into tall crystallizing vessels; the potassium chloride, which crystallizes out, still contains sodium chloride, magnesium chloride, and very small quantities of magnesium sulphate. These impurities are removed by placing the salt in wood or iron vessels with perforated false bottoms, pouring water over, allowing to rest for some time, and running off the resulting potassium chloride solution, which is used to dissolve fresh carnallite. As a rule, another similar treatment follows, when a salt of 90 per cent strength is obtained. The potassium chloride is then freed from the adherent moisture, either by calcination in kilns heated by the waste heat from evaporating pans, or on iron plates heated by steam. The mother liquor left after the crystallization of the potassium chloride, which still contains considerable quantities of that salt, is concentrated in evaporating pans. The salt which separates during the evaporation is generally calcined and added to the manurial salts. Formerly the liquor was several times evaporated to a small extent and left to crystallize after each evaporation. Now, in consequence of the fall in prices, it is only evaporated once, but as far as can be done without much injury to the pan—as a rule, to 35° B. From the clarified liquor artificial carnallite separates on cooling; the residual mother liquor is either run to waste or worked up for bromine, or it is evaporated to 40° B. and run into barrels, in which the magnesium chloride solidifies. The artificial carnallite serves as a source of very pure potassium chloride. It is dissolved in hot water to form a solution of 34° B., from which coarse potassium chloride crystallizes on cooling. The crystals are treated in the same manner as the first crystallization from the crude potash salts, when a very pure product results.

The second and more recent method for treating natural carnallite is founded on the fact that hot magnesium chloride solution takes up the total content of the natural impure carnallite and deposits it again in the crystalline state on cooling, in a very pure condition, so that on decomposition with water it produces very pure potassium chloride. The mother liquor is again applied to the solution of fresh quantities. The mother liquors resulting from the decomposition of the artificial carnallite are evaporated, when they deposit small quantities of "stage salt" and give a fresh crop of carnallite. The process offers great advantages: pure potassium chloride is obtained, and there is less liquor to evaporate; but, on the other hand, it requires complicated machinery.

The residue obtained in working up the saline deposits for calcium chloride, amounting to about 30 per cent of the crude salts, is sold to green glass-works under the name of "glass melt". It is there well dried, finely ground under edge runners or in a roller mill, and is then best at once mixed with the other substances used in the charge. The air-dried residue contains: potassium chloride, 5.85 per cent; sodium chloride, 47.0 per cent; magnesium chloride, 3.85 per cent; magnesium sulphate, 29.25 per cent; insoluble matter, 8.15 per cent; water, 6.50 per cent.

G. Borsche, of Leopoldshall, near Stassfurt, has patented a process for the preparation of potassium sulphate from kieserite and potassium chloride. A mixture of 5.8 equivalents of potassium chloride and 4 equivalents (2 molecules) of magnesium sulphate is treated in succession with small quantities of cold or moderately warm water, insufficient to dissolve the salts completely. For example, 6 equivalents = 447 grms. of KCl and 4 equivalents = 920 grms. of $MgSO_4 \cdot 7H_2O$ are treated four times in succession, each time with 300 grms. of water, after each digestion the liquor being allowed to drain away. The residue is then almost pure potassium sulphate, and there is in all about 1200 grams of water to evaporate, leaving an impure magnesium chloride.

CHAPTER XLVI.

GOLD AND SILVER WASTE.

Extraction of Gold from Tailings.—In the extraction of gold from its ores either by amalgamation or by chlorination a considerable quantity of tailings were produced and accumulated to form great mounds. In the McArthur Forrest process of gold extraction it was found that these tailings could be profitably treated for the recovery of even the small traces of gold which they contained, with the result that all these heaps have been re-worked and many companies have earned through this means quite a respectable profit. Shortly, this process consists in treating the pulverized ores or slimes with a weak solution of potassium cyanide which dissolves out the whole of the gold, the liquid is caused to percolate through tanks containing boxes filled with fine scrap zinc, which causes the deposition of the gold in the form of a fine powder. This is perfectly pure gold and requires only to be melted and cast into bars to be ready for the mint.

Recovery of Gold from Liquids Containing the Metal.—Boettger¹ brings the liquid to the boil in porcelain vessels, adds a solution of stannous oxide in caustic soda, and continues the boiling until all the gold—in combination with tin—has separated as a fine, intensely black precipitate, which is pressed and then dissolved in *aqua regia*. The liquid thus obtained is a solution of gold and stannic chlorides; it is carefully evaporated, diluted with distilled water, a sufficient quantity of sodium potassium tartrate (Rochelle salt) added, and the mixture warmed, when every

¹ "Dingler's Journ.," 213, p. 257; "D. Ind.-Zeit.," 1874, p. 296.

trace of gold separates as a very soft brownish powder, whilst the tin remains dissolved.

Recovery of Gold from Electro-gilding Baths.—According to Plage,¹ a porous cell containing a solution of salt is placed in the gold solution; inside the cell is placed a zinc rod, which is connected by a brass wire to a thin brass plate immersed in the gold solution. In three to four weeks, after once or twice renewing the brass plate, the zinc rod is dissolved, and all the gold is precipitated on the brass. The latter is dissolved in nitric acid in a porcelain dish, the gold is washed, dried, and finally melted with saltpetre in a Hessian crucible.

Recovery of the Gold from old Photographic Toning Baths.—P. Haugk² filters old gold baths into a white glass bottle, adds excess of sodium carbonate, and then an alcoholic solution of magenta, drop by drop, until the liquid has become raspberry-red. If the flask is now placed in a light window, the gold is entirely precipitated in six to eight hours, so that the liquid may be poured off. When a sufficient quantity of the precipitate has collected by repeating this process, it is well washed and brought on to a filter, which is burnt, and the gold then dissolved in excess of *aqua regia*. By evaporation of the solution, gold chloride is obtained, which may at once be again used for photographic purposes.

Collection, Reduction, and Purification of Silver and Gold Residues.—Complete instructions for these operations have been given by J. Krüger,³ taking all photographic waste of this description into account, and showing exactly how the highest yield may be obtained from all residues, and the processes best conducted with the ordinary technical appliances.

1. *Liquids which Contain Noble Metals.*—If we follow the numerous photographic operations in the collodion and silver printing processes, we obtain the following residues: (a) Old, exhausted, and useless silver baths; (b) developing

¹ "Industriell.," 1878, p. 190.

² "Photog. Arch.," 1877, p. 6.

³ "Neueste Erfindungen," 1878, p. 194.

and intensifying solutions; (c) fixing baths; and (d) the wash waters of these operations; (e) the wash water of the silver prints; (f) old gold baths; (g) old fixing baths; and (h) the wash waters after fixing. At first sight it is evident that these solutions differ principally by containing the silver in quite different compounds and forms—partly in solution, partly suspended, partly reduced, partly dissolved as double compounds. On this account it is advisable only to mix liquids of the same kind, and not, as is often done, to bring all together. Thus all old silver baths should be kept separate, as also the intensifying liquids and the solutions and wash waters containing sodium hyposulphite; for by mixing, not only is the separation of the silver made more difficult, but also a considerable loss is entailed. Accordingly, we shall consider these liquids one by one, and inquire how they may be simply, cheaply, and easily worked up for recovery of silver.

(a) *Old Silver Baths.*—The silver bath used in the negative process finally contains, when it is completely exhausted and saturated with silver iodide, the silver in the form of mixed compounds; it is principally the compound of silver iodide and nitrate ($\text{AgNO}_3 + \text{AgI}$) which makes the reduction, or rather the recovery, difficult. Many photographers adopt an easy course by simply evaporating these baths to a strength of one part of silver salt to ten parts of water, at once using this solution to silver albumin paper. It should be remembered, however, that the silver iodide, which is dissolved in the solution, and is thus conveyed to the albumin paper, does not give brilliant whites and pure tones. It should not be overlooked that even by a long-continued fusion of the residue of salts produced from these old negative silver baths, the silver iodide therein can neither be separated nor reduced, but rather remains, and can only be destroyed by the decomposition of the double compound. The most general method for separating all the silver salt contained in these baths is to add to them common salt or hydrochloric acid, so long as a precipitate is produced, the silver being thus precipitated as

chloride. This precipitation occurs completely under all circumstances, and hence no objection could be taken to the process, except that the silver chloride obtained is more difficult to reduce and smelt than is the carbonate. For if, in place of common salt, pure soda (sodium carbonate) is used for precipitating the silver, then silver carbonate is obtained, which has many advantages for our purpose of reduction: it deposits more rapidly, and is more easily and quickly reduced, since it does not froth up so much as silver chloride in the fusion. The same process is used with the soda solution as with the common salt solution; the mixture is vigorously stirred, allowed to clear, and then more precipitant added so long as a precipitate is produced. It might be objected that sodium chloride only precipitates silver, whilst soda also throws down other metals. But this is not material, since in the silver bath neither iron nor copper nor similar metals are to be found; and the small quantities of cadmium derived for the collodion are either taken up by the slag in the fusion or burnt away. The silver carbonate thus obtained is a pale yellow powder which is easily reduced; it requires in the fusion only a small addition of sodium carbonate as flux, in order to obtain a pure regulus.

(b) *The Developing and Intensifying Liquids.*—These liquids are more or less dark in colour, according to the chemicals employed; the precipitate which forms in the liquid is also of varying purity. It always consists essentially of reduced silver, which is precipitated more or less pale in colour according to its purity. It is collected, washed, dried, and fused with a little soda alone, when it gives a solid button of metallic silver. Every photographer who carefully collects these liquids will be well rewarded for his labour in the recovery of the silver, the profit more than repaying the trouble. This precipitate may be smelted together with the precipitate of silver carbonate obtained from the old silver baths.

(c) *Fixing Solutions and their Wash Waters.*—In view of the difference between the fixing salts—potassium cyanide

and sodium hyposulphite—it is, in the first place, important to keep the two separate, and also the corresponding wash waters. In the case of potassium cyanide, which is mostly used for negatives, two methods may be adopted in order to recover the silver: the liquid may either be evaporated to dryness, and the residue ignited, or it may be treated with pure hydrochloric acid, so long as a precipitate is formed. On account of the extremely poisonous hydrocyanic acid gas evolved in the latter operation, it must be conducted in the open air, or under a chimney with a good draught. The potassium cyanide is then decomposed, potassium chloride is formed, and the dissolved silver is precipitated. In evaporating—which may be done in summer in the air—in a hot, draughty room, the potassium cyanide decomposes spontaneously; finally, a formate is produced, and there remains a dark brown mass of salts, from which all the silver may easily be obtained by fusion. It is highly to be recommended to allow all potassium cyanide solutions, from which silver is to be recovered, to decompose spontaneously in the air, by which they lose their poisonous properties and separate a large portion of the silver.

Old hyposulphite baths and their wash waters are generally collected and sold, but naturally something must then be lost, and it is at least advisable to know the amount of silver in the liquid. This is simply found: exactly 100 grms. are measured off, diluted with 200-300 grms. of water, and a strong potassium iodide solution added, so long as a precipitate is formed. This precipitate is silver iodide; after washing and drying, it is weighed and the corresponding quantity of pure silver calculated. This may be done by means of the following table:—

2·176 parts of silver iodide = 1·000 part of metallic silver.	
1·958	" " = 0·900 " "
1·741	" " = 0·800 " "
1·520	" " = 0·700 " "
1·305	" " = 0·600 " "
1·088	" " = 0·500 " "
0·870	" " = 0·400 " "
0·653	" " = 0·300 " "
0·435	" " = 0·200 " "
0·217	" " = 0·100 " "

This method depends on the insolubility of silver iodide in weak solutions of sodium hyposulphite. As a rule, however, it will be found that, on long standing, sodium hyposulphite separates a portion of the silver chloride dissolved in it. Silver sulphide is deposited both at the bottom, where it forms a black mud, and on the sides of the vessel, which must be remembered in emptying the contents. The silver sulphide, which is not an insignificant amount in old hyposulphite baths long exposed to the air, is calculated to the corresponding quantity of silver by the following table:—

Silver Sulphide. Parts by weight.	Metallie Silver. Parts by weight.
1.148	1.000
1.033	0.900
0.918	0.800
0.804	0.700
0.689	0.600
0.574	0.500
0.459	0.400
0.344	0.300
0.230	0.200
0.115	0.100

The method, recommended by several writers, of decomposing these old hyposulphite baths by hydrochloric acid, in order to obtain the dissolved silver as silver sulphide, is not considered advisable by the author, for, on the one hand, the sulphuretted hydrogen gas which is evolved is extremely dangerous to health, and very harmful to all photographic work (on which account the operation must be performed at a distance from the studio and in the open air), and, on the other hand, so much sulphur is separated that its removal necessitates a separate operation, making much more difficult the further treatment of the precipitate. Such precipitates containing sulphur can only be reduced by fusion, and since in this case the addition of pure soda or other salts does not suffice, iron must be added to the mixture in the form of wire or nails, or as filings, so that sulphide of iron may be formed and the difficultly reducible silver sulphide obtained pure. Under all conditions the utilization of these liquids by the method just mentioned is as complicated as it is unpleasant, hence sale is the more

advisable method of disposal. In the author's many years' practice he has endeavoured, in face of these obstacles, to discover a simpler process, which would be neither too costly nor too complicated for the photographer. The best results may be obtained by the process next described.

A large wooden vessel, in which all old hyposulphite baths and wash waters are collected, is provided with a series of plug-holes, in a vertical line, at distances 5 cm. (2 ins.) apart, from the top to immediately above the bottom. All the holes are closed by well-fitting corks. A broad, clean strip of zinc, wound round with a fairly strong copper wire, and long enough to project out of the liquid, is brought into this vessel. When this copper-zinc couple has stood for some time in the liquid, the latter will be found to have become quite colourless, whilst the surfaces of the metals are covered by a grey metallic powder, which can be readily loosened and wiped off. This consists of metallic silver, which partially sinks to the bottom and partially adheres to the copper and zinc; in quantity it is equivalent to the metals dissolved. This precipitated silver is certainly not chemically pure; it contains zinc and copper, but their presence offers no difficulty in the subsequent fusion process. The separation of the silver from these liquids by phosphorus is very efficient, but costly; on the large scale it would be difficult, if not impossible, of execution. The addition of green vitriol, which the author also tried, is not without effect, but the silver precipitate then appears deep black in colour and contains sulphur and sulphide of iron. Copper sulphate (blue vitriol) behaves in the same manner. The organic acids, such as gallic and pyrogallic, are partly inefficient, partly too expensive. More certain and less costly, though large vessels and much water are required, is the precipitation of the silver by potassium iodide, as given above, since weak decomposed hyposulphite solution cannot dissolve silver iodide.

The utilization of old liquids containing gold will be considered afterwards. In the next place, we shall see how the silver precipitates are to be further treated; but before

going on to the necessary processes of fusion or smelting, the methods for treating solid residues containing silver, before fusion, are given.

2. *Solid Residues Containing Silver*.—Under this heading come—(a) old silver filters; (b) old enclosures in the plate box, also the paper wrappings on the prepared plates, etc.; (c) clippings from the prints. In order to reduce the volume of these papers, they are first burnt, in which operation it is advisable to sprinkle fine, dry, powdered saltpetre over the glowing mass, by which a slight explosion is caused and a more complete combustion of the carbonaceous matter of the paper (and, in albumin papers, of the albumin) is effected. It not rarely happens in this operation that the silver is obtained in the form of very fine minute globules of metal. This is not the object of the process, but simply, by diminishing the volume of the material, to save space, and thence expense and inconvenience. These ashes may then be at once mixed with the silver precipitates obtained from the various liquids, so that they may be reduced together. With this we reach the second part of our process—the smelting out of the silver. The author does not think it necessary to state to what extent this operation may be performed by the photographer himself, but simply observes that many are of the opinion that this smelting may be accomplished in an ordinary iron stove, and even maintain that the best results are then obtained. That this is not altogether unwarranted will appear in the following pages, but it must be at once understood that this troublesome and dangerous operation has not for its object the obtaining of some reduced silver as a regulus, but to regain the whole of the silver united in one lump, and that with the least possible loss.

Smelting Out of Silver.—In whatever form the silver is collected, it must, in the first place, be thoroughly dried, either by spreading out and leaving in the air, or, in case that is not sufficient, by artificial heat. Care must be taken to see that this drying is thorough, for if the residues are

thrown into the heated crucible while still moist, it would almost certainly crack, which is to be avoided. In every smelting operation two things are required—the complete reduction of the metal and its union to one lump, on which account certain substances require to be added. This addition consists almost always of an alkali salt, a carbonate, nitrate, or tartrate, i.e. a compound, which can both separate the silver compound to be reduced and also itself readily fuse, so that the silver, produced in small globules, may separate completely, sink to the bottom of the fluid mass, and there amalgamate. If we have to do with pure silver masses, such as result from the developing and intensifying solutions, and also with silver carbonate, the smelting process proceeds calmly, exactly, and rapidly, whilst silver chloride, and silver sulphide to a greater extent, render the process difficult.

The fluxes used and proposed for these operations are as little of the same nature as is the residuum or the waste resulting from the various photographic operations. The following salts are chiefly employed for this purpose: potassium and sodium carbonates, common salt (sodium chloride), sodium baborate, and also the so called "black flux," a mixture of potassium carbonate, and carbon. These salts differ essentially in their action on the metals to be reduced. The alkaline carbonates are reducing agents and also excellent fluxes. They take up the chlorine, bromine, sulphur, etc., giving off carbon dioxide and forming the corresponding potassium and sodium salts, with the formation of a light flux, which dissolves accidental impurities, such as iron, copper, lead, and also calcium salts, and separates completely purified silver. They are the most often used, and since it is desirable to combine the advantages of the potassium salt with those of the sodium salt, since together they form a readily fusible glass, the latter is better to handle since it can readily be converted into a dry powder, whilst the potassium salt is very deliquescent; frequently the two are mixed, two parts of sodium carbonate being well ground with

three parts of potassium carbonate. The alkaline nitrates have an oxidizing action on the base metals present, and also effect the complete combustion of carbon. Both are used in refining the noble metals, small quantities being added to the carbonates in order to obtain purer gold and silver. The nitrates are not used alone. Borax acts in a similar manner to the nitrates, not by oxidization, but by forming glassy fluxes with most of the base metals, i.e. it dissolves them, so that they are completely converted into a coloured glassy slag. It is thus equally useful in refining, and is also valuable because it is easily fusible, soon bringing the slags into a very fluid state, by which the separation of the noble metals is much facilitated. Borax is generally used towards the end of the smelting process, in order to increase the purity of the silver and gold and help them to melt together. Common salt, which is valued by some, is only useful on account of its ready fusibility. It is not correct to say that common salt reduces silver chloride; it simply serves as a flux to fuse together the particles of silver, for which it is very suitable, because it easily becomes fluid, and under those conditions the silver can readily collect without any loss of the metal. For this purpose the author can recommend it from his own experience. Under the name of "black flux" a preparation is known which formerly was almost exclusively used in smelting the noble metals. As already mentioned, it consists essentially of potassium carbonate and organic carbon; it is obtained by mixing two parts of potassium bitartrate with one part of saltpetre and setting the mixture on fire by means of a red-hot coal. A slow explosion occurs, with the production of much smoke; finally, when the mass is quite burnt and has cooled, a black carbonaceous mass remains which is black flux. This mass is ground while still warm and at once brought into well-closed glass bottles, in order to prevent it absorbing moisture from the air, which it would rapidly do on account of its deliquescent nature. In addition to these salts, which, however, are always sufficient in a stove with a good draught and sufficient fuel, it has been recommended

to add rosin, sugar, and even soaps and syrup, as reducing agents, but the author does not agree with this advice, for what cannot be accomplished by the salts will never be attained by means of these easily decomposed organic matters.

We now come to the charging of the crucible. Melting crucibles are conical vessels of fire-clay. The clays used for most vessels for industrial purposes are not of such a composition that they can be used for melting crucibles. It is necessary to impart to them the requisite resistance to heat by certain additions. The conditions required are twofold: indifference towards the fused mass, and durability at high temperatures. A clay which possesses these properties when mixed with half its weight of coarse sand is that mined at Almrode, from which are obtained the Hessian crucibles used all over the world. In spite of their durability in the fire, these crucibles require a certain amount of care, since they are not suitable for the fusion of all substances. Thus they cannot be used for the fusion of those compounds which are able to dissolve quartz (silicic acid) and thus form silicates. In this case the walls or the bottom of the crucible may become perforated, so that the fluid contents may drop or flow out. To these substances belong free alkalies, free bases, and metallic compounds which form glasses with silica, as, e.g., litharge. For crucibles in which this substance is to be fused, in place of the quartz an addition is made of finely ground fireproof pottery to the clay. Other manufacturers take for this purpose also difficultly combustible carbon, such as graphite and coke. Another kind of crucible is the Passau crucible, made from one part of plastic clay from Schildorf, near Passau, with two or three parts of an impure graphite from the same district. These crucibles may, without danger or the least alteration, be heated up to 150° Wedgewood. They resist changes of temperature extremely well, and have the particular advantage over all other crucibles of a similar kind that the inside is quite smooth, which is of great advantage and importance in smelting the noble metals, since then the fluid slag can be poured out clean and

without sticking to the sides of the crucible. If this crucible has not the fame of the Hessian, it is because it is too dear for those processes in which the melting vessel is broken after cooling at the end of the operation. In conclusion, it is to be noted that all crucibles soon become useless; even if they are not cracked it is not safe to use them for any large number of fusions. Crucibles made largely of graphite are also manufactured in England by the Morgan Crucible Co. of Battersea, and are excellent for this purpose.

The crucible is filled in the following manner: The silver ashes, residues of the developing process, and salts precipitated in the form of silver carbonate are, in a perfectly dry condition, well mixed with the additions, which for this purpose are, say, potassium carbonate three parts, sodium carbonate one part. If, after thirty minutes' heating, the mass is near fusion, one part of saltpetre is added. Equal parts of silver ashes and the flux are taken. The crucible should at first be at most two-thirds full, and it is advisable to cover the contents with a thin layer of common salt. If pure silver salt residues are melted together without the ash constituents, a mixture of equal parts of common salt and potassium carbonate is sufficient. When the mass melts, a very little dry powdered saltpetre may be added. Old collodion films, with and without varnish, both before and after fixing, contain silver bromide and iodide, and are therefore less easily reduced, yet a mixture of potassium carbonate four parts, sodium carbonate one part, and sodium chloride one part, added in equal quantity, will effect the reduction if a fierce and regular fire be maintained.

Silver sulphide is the most difficult to reduce, yet the operation is easy if it is heated with an equal weight of the following mixture: sodium carbonate, 3 parts; common salt, 1 part; iron filings, $\frac{1}{2}$ part. An excellent reducing agent for silver sulphide is potassium cyanide, equal in weight to that of the sulphide. Potassium sulphocyanide is then produced, and chemically pure silver separated.

Silver chloride, which the author avoids when possible,

may be reduced by the method given for collodion films, in which it is advisable to apply the common salt by sprinkling it into the crucible.

In all these mixtures care should be taken that the separate parts are quite dry and that the crucible is at first only three-quarters full. After charging the crucible, it may be placed in the stove. In the first place, a circular tile, of the circumference of the crucible—but not greater, so that the draught is not restricted—is laid on the fire-grate. The crucible is then placed upon it, surrounded by wood, and the latter lighted. As soon as it is sufficiently ignited, the wood and the crucible are covered with charcoal and coke, care being taken that the fire is always close round and covering the crucible. A long iron poker is used to stir the fire when required. All the fuel must be dry, the crucible always well surrounded and covered. When the first charge of the crucible is quite fused, small portions of the residues are taken, wrapped in a piece of paper, and the ball brought into the fluid mass. A slight frothing follows, but in a short time the contents of the crucible are again in quiet fusion. The addition of fresh portions is continued in the same manner until the whole is introduced. With some care and attention frothing over need not be feared; if the mass rises considerably it is stirred with a cold poker, when it at once falls. After the addition of the last portions the fire is brought to its fullest heat, well stirred, new fuel added, and efforts made to reach the highest temperature. This can be done in half an hour.

When it is thought that the reduction is finished the fused mass of salts is examined, both as to its appearance—since it must be at a white heat and quite fluid—and by means of an iron wire, which is plunged into the melted mass, and a test taken. The wire becomes covered by slag, which is examined with a lens to see whether fine, scattered globules of silver are present in it. The slag should also be clear, and neither rough nor sandy, which would indicate that the mass is not yet sufficiently fluid to allow these impurities

to settle. If the test shows any defects—and especially that the silver has not completely separated and united to one mass—the fire must be increased, and the contents of the crucible again properly fused for some time, which is continued until a new test shows the requisite signs of complete reduction and collection of the silver. This result is occasionally attended by difficulties, and, in fact, always when the stove is not provided with a sufficiently good draught or the necessary dampers, for even with sufficient fuel the necessary heat cannot be attained without a good draught.

When the operation is successfully finished the crucible is taken out with the tongs and placed on a heated stone slab. The silver may be removed either by pouring the whole contents out or allowing to cool. If the material is poured out, it may be run into an iron vessel—say a mortar—well greased with tallow, and, after completely cooling, the contents should be knocked out, and the silver freed from adherent impurities.

If, on the other hand, the crucible is allowed to cool slowly, the silver and slag adhere to it; the cold crucible is then broken, and the silver obtained as a rounded compact lump, free from slag. An attentive worker will always obtain a successful result by carefully following these directions; but a certain amount of practice, and the knowledge thereby gained, are of great advantage. A beginner should never throw away the slags without previously examining them for silver. This is done with the lens, and also, more certainly, by dissolving a small portion in hydrochloric acid, which does not attack metallic silver. If the slag is found permeated with silver, it must be again fused at a higher temperature.

Recovery and Smelting Out of Gold.—All liquids which contain gold are collected, and, if alkaline, acidified with strong hydrochloric acid. Any precipitate produced is disregarded. To the acid liquid is then added a strong solution of ferrous sulphate and heat applied, so long as it produces a precipitate. Excess is not injurious, but the liquid ought not to be very acid. After a short time a black precipitate of

reduced gold settles to the bottom, and is carefully filtered. If there is plenty of time, the precipitate may be allowed to deposit completely, and only the last portions filtered. When all the clear liquid has been poured off. The residue on the filter is washed several times by pouring clean water over it, and then dried. When this is done the filter is burnt over an open flame, the ash and its contents collected, and both put in a porcelain mortar with double the weight of pure (anhydrous) sodium carbonate; the mixture is then again brought into a crucible of suitable size.

The crucible must have double the capacity of the

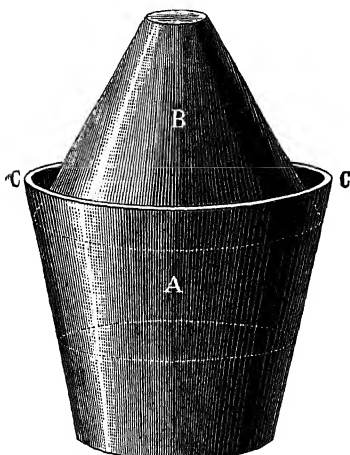


FIG. 22.

The whole apparatus, as arranged, is placed on a piece of stone in a wine cask, then surrounded by a layer of coal; as soon as the fire is burning strongly the crucible is covered with coal, and a strong white heat maintained continuously. The process is finished after about two hours; the fire is then removed, the crucible allowed to cool, and then opened, when the lump of gold is found at the bottom.

This is the simplest and safest method; it deserves preference because, if foaming and frothing should occur, no trace of metal can be lost. The little apparatus is recommended for smelting silver residues.

Photographic Paper Refuse: Filters.—This will

incinerated, and the ash treated with dilute nitric acid. The liquid is then filtered, and the silver precipitated by copper. The ash may also be digested with strong hydrochloric acid free from nitric acid, and the washed and dried residue fused with its own weight of soda and about 10-15 per cent of saltpetre. The metal obtained is then dissolved in nitric acid, when a residue containing gold may remain. This residue is dissolved in *aqua regia*, the solution diluted and precipitated by green vitriol; the gold obtained is washed, dried, and melted with saltpetre and borax.

In regard to the method just given, in which the silver is separated by copper, it is to be observed that in the Frankfort Gold and Silver Separating Works the silver obtained in sulphuric acid solution is precipitated by iron instead of copper. The objections to this process are: the loss through the evolution of hydrogen, the simultaneous precipitation of copper, and the contamination of the silver by phosphorus, silica, etc., from the iron. The objections are, however, removed by allowing the silver sulphate solution, with the addition of water, to crystallize, and then reducing the crystals by scrap iron. The crystals are stirred with water, and iron gradually added, so that every trace of silver is precipitated, whilst copper remains in the original solution. The impurities contained in the iron go into the slags produced when the silver is fused, so that the latter is obtained in a purer state than when copper is employed. The principal advantages of this method are: economy in acid, the mother liquors from the crystals being returned to the dissolving vessel; avoidance of the purchase of copper, the cost of which is not repaid by the blue vitriol obtained; and economy in steam, since the solution becomes very hot spontaneously.

CHAPTER XLVII.

PLATINUM RESIDUES.

1. *The Residue which Remains after Treating the Crude Ore with Aqua Regia.*—In a clay crucible with a thick bottom, 1 part of the platinum residue (300-400 grms. at the most in one operation) is fused with an equal weight of granulated lead and 1.5 part of litharge, or with 1 part of granulated lead and 2 parts of a flux, consisting of 1 part of fluorspar and 1.7 part of anhydrous gypsum. The mixture is stirred with a pipe stem, the crucible broken and allowed to cool, when the lead regulus is carefully freed from the slag and dissolved in hot, fairly strong nitric acid; the platinum metals which remain undissolved are treated as described under 3 (c). Since a little palladium has dissolved with the lead, the latter is precipitated by sulphuric acid, the solution evaporated to dryness, the residue dissolved in water, filtered, and the palladium precipitated from the filtrate by mercuric cyanide.

2. *The Residue of Impure Ammonium Chloroplatinate* obtained on concentrating the liquid, from which the greater part of the platinum has been precipitated, is essentially the chloroplatinate.

3. *The Solution Filtered off from the Impure Ammonium Chloroplatinate*, which is either evaporated to dryness and the residue ignited, or from which the metal is precipitated by iron or zinc, is especially rich in rhodium.

Wöhler has recommended the following method for the separation of the metals:—

(a) *The Impure Ammonium Chloroplatinate* (2) is reduced by ignition, the metals dissolved in *aqua regia*, the solution evaporated almost to dryness, taken up in a little water, mixed with twice its volume of spirits of wine, and a saturated

solution of potassium chloride added. The precipitate consists of the potassium double chlorides of platinum and iridium, with traces of rhodium and palladium. It is filtered off and washed with alcohol containing potassium chloride. After drying, it is brought into a porcelain crucible, where it is well mixed with its own weight of sodium carbonate. The filter is burnt, and the ash added to the mixture. The mass is then gently heated until it becomes black throughout. The platinum is thereby reduced, but palladium, iridium, and rhodium oxidized. The mass is extracted with water, the potash withdrawn from the oxides by means of hydrochloric acid, and the whole washed, dried, and ignited; it is next, in order to separate the rhodium, fused with six parts by weight of potassium bisulphate at a gentle and long-continued heat. The rhodium salt which is formed is extracted with water, and the yellow solution boiled with hydrochloric acid, when it becomes red owing to the formation of the chloride. Caustic potash precipitates from this solution brownish-red rhodium hydroxide, which is reduced to metal by ignition in a current of hydrogen. The residue of platinum, palladium oxide, and iridium oxide is reduced by heating in a current of hydrogen, and, after cooling, treated with nitric acid, which dissolves the palladium. The liquid is neutralized by sodium carbonate, and a solution of mercuric cyanide added, when palladium cyanide is precipitated, which, after washing and drying, only requires ignition to be converted into metal.

A mixture of metallic platinum and iridium oxide remains. It is digested with dilute *aqua regia*, which extracts a portion of the platinum, the clear solution is poured off, saturated with ammonia, evaporated to dryness, and carefully ignited, when pure platinum remains. The residual iridium oxide containing platinum is evaporated to dryness with sodium chloride and *aqua regia*; the platinum salt is extracted from the residue by water, whilst the iridium oxide remains undissolved. The latter is filtered off, washed first with common salt solution, then with ammonium chloride,

dried, ignited, and reduced to metal by heating in a stream of hydrogen. The filtered solution contains a small quantity of iridium, which is separated by evaporating to dryness, heating the residue, as above, with sodium carbonate, and extracting the platinum from the washed residue with dilute *aqua regia*.

(b) *The Liquid Filtered from the Impure Ammonium Chloroplatinate, or the Metals Precipitated therefrom by Iron or Zinc.*—The metallic powder is dissolved in *aqua regia*, and then treated in the same manner as the filtered liquid, which is evaporated to dryness, the residue digested with strong *aqua regia*, potassium chloride added, and the solution evaporated to dryness on the water-bath. Ferric and copper chlorides are then extracted by alcohol, the residual double chlorides of rhodium, palladium, and iridium are fused with potassium bisulphate, and the mass treated with water, when iridium oxide remains. The liquid contains palladium and rhodium; the former may be precipitated by mercuric cyanide, and then the latter with potash, after boiling with hydrochloric acid; as in (a).

(c) *The Residue Insoluble in Aqua Regia.*—The black levigated mass is intimately mixed with about an equal volume of ignited and finely ground sodium chloride, and the mixture heated in a porcelain or glass tube in a slow current of moist chlorine, until the gas begins to pass through unabsorbed. The further end of the tube opens into a well-cooled, tubulated receiver, from the tubulure of which the excess of chlorine is passed into alcohol. The double chlorides of sodium with iridium and osmium are produced; the latter is mainly decomposed by the moisture in the chlorine, the resulting osmic acid sublimes into the receiver, and is partially carried into the alcohol. After cooling, the residue in the tube is treated with water, and then washed with hot water. The dark reddish-yellow iridium solution, filtered off from the ferric oxide, is mixed with strong nitric acid and distilled, when more aqueous osmic acid passes over. When the liquid has in this manner become very concentrated, it is mixed

hot with a strong solution of ammonium chloride. On cooling, a large portion of the iridium separates as the crystalline blackish-red ammonium iridium chloride, which is filtered off and several times washed with ammonium chloride solution. On ignition it yields a grey sponge of iridium. A small quantity of platinum in this salt is detected by grinding it very fine, mixing with eight times its quantity of water and leading in sulphur dioxide, when the iridium salt dissolves, leaving the yellow platinum salt. The residual solution is mixed with soda crystals in excess, evaporated to dryness, the mass gently ignited in a crucible, and, after cooling, extracted with hot water, which generally becomes coloured yellow by alkaline chromate. The black powder which is left consists of a compound of iridium sesquioxide with soda, contaminated with ferric oxide. It is reduced by gentle heating in a current of hydrogen, after which water extracts caustic soda, and the iron is removed by digestion with strong hydrochloric acid. If the residue be then digested with very dilute *aqua regia*, a little platinum is generally extracted, and may be precipitated by ammonium chloride.

In order to extract ruthenium, the iridium must then be fused for at least an hour in a silver crucible with a mixture of potassium chlorate and caustic potash. The mass is treated with water, the yellow solution of potassium ruthenate, which has been allowed to clear by settling (not filtering), is poured off, the residual iridium oxide repeatedly washed by decantation, and the solution of potassium ruthenate neutralized by nitric acid, when black ruthenium sesquioxide is precipitated. The latter is reduced to metal, in the same manner as the iridium oxide, by heating in a current of hydrogen.

The iridium, after this purification, is strongly compressed and subjected in a crucible to the fiercest white heat, when it is obtained in a somewhat coherent and dense condition.

The platinum residue, after one such treatment, is not exhausted; further quantities of osmium and iridium can be obtained by repeating the same operations.

CHAPTER XLVIII.

IRIDIUM FROM GOLDSMITHS' SWEEPINGS.

D'HENNIN removes the iridium from goldsmiths' sweepings containing that metal¹ by fusing 12·5 parts with 3 parts of sodium arsenate, 18 parts of black flux, and 20 parts of ordinary flux—borax, tartar, charcoal, and litharge—and separating the lead regulus containing the gold and silver from the upper layers of iron-grey lumps consisting of iron, iridium, and arsenic. In France (according to Muspratt) large quantities of this refuse are worked up; they come from America, principally from Californian gold, which often contains osmiridium. By repeatedly melting gold alloyed with copper, according to Wilson, the osmiridium separates almost completely. According to Dubois, the Californian gold is melted with 3 parts of silver, when the osmiridium deposits from the alloy which has a specific gravity of 12-13.

¹ According to "Dingler's Journ."

CHAPTER XLIX.

METAL WASTE.

Recovery of Brass Waste.—In order to separate mixed filings, it was usual to remove the iron and steel by means of a magnet held in the hand, when the brass filings remained. Vavin, a French engineer, has constructed a machine to shorten this tedious operation.¹ It has already been tried in practice, and is made by Cail & Co. of Paris.

This machine consists of two drums, rotating on their axes, and placed one above the other. The surfaces of the drums are covered with alternate strips of soft iron and copper. Each iron strip is suitably connected with a series of horse-shoe magnets, which are so arranged that the one pole of the magnet is in contact with one iron strip, the other pole with the next. The mixture of metal filings is contained in a hopper with a vibrating foot, from which the filings fall in a stream nearly as wide as the drum. The iron filings are attracted by the iron strips of the drum, which are made magnetic, and are carried away by them until they are swept off into a receiver by a revolving brush. The brass filings and a portion of the mixture of the two metals fall upon the second drum, which is similar in construction to the upper drum, but is so placed that the iron and copper strips are in such a position to those on the upper drums that strips of different metals always come into the same vertical plane. Whilst now the brass filings fall straight off, the separating process is completed by the iron filings attached to the surface being removed by the cylindrical brush on the other side and swept into the receiver. The machine is driven by hand or

¹ "Engineering"; "Dingler's Journ.," 197, p. 18.

from shafting; it requires a floor space of only 2 ft. 6 ins. by 1 ft. 2 ins., and a height of 5 ft. 3 ins.

The same end is attained in a very simple and economical manner at the London and North-Western Railway Works at Crewe by a process of fusion.¹ The mixed iron and brass borings and the slags from brass-casting are mixed with limestone, powdered coal, and oxide of iron, or hammer scale. This mixture is heated, when the brass separates at the bottom of the fluid slags, and is run into ingot moulds.

Bronze Pigments from Alloy Waste.—The manufacturers of imitation gold-leaf employ for this purpose the waste obtained in hammering and rolling. In the older processes² the waste from the manufacture of imitation gold-leaf is ground with honey or gum-arabic solution on a slab by a muller, until a perfect mixture is obtained. The paste is brought into water, in which the binding medium dissolves, whilst the metallic powder, after drying, is subjected to the oxidizing process. For this purpose the dry powder, mixed with a little fat, is brought into a pan and heated over an open fire until the mixture has acquired the desired shade.

At the present time this process has been shortened by the use of machinery. The proper alloys to produce certain colours, the shade of which can be obtained without oxidizing, are made by melting together the metals in the correct proportions. The alloys are then beaten out into very thin sheets by hammers driven by steam-power; the sheets are converted into powder by bringing them upon fine iron-wire sieves, and rubbing them through the meshes of the sieve by a wire brush. This rubbing is accomplished under a continuous addition of oil; the mass which flows away from the sieve is then brought into a grinding-machine of peculiar construction, in which the metal particles are very finely ground. The mill consists of a steel plate, thickly studded with fine blunt-pointed needles, turning over another steel plate.

The alloys are thus obtained in the form of a very fine

¹ "Engineering;" "Dingler's Journ." 205, p. 384.

² "Die Legirungen," A. Krupp: Vienna, Hartleben.

powder mixed with oil. The mass is first brought into water, when the greater part of the oil rises to the surface, and, on subjecting the metallic mass at the bottom of the vessel to a very high pressure, almost all the remainder of the oil is removed.

The variety of bronze pigment known as "brocat," consists of somewhat coarser pieces of the alloys, which are generally obtained from the leaf metal by powdering under stamps and separating the pieces of unequal size—first by sieves, afterwards by a current of air. One species of "brocat" consists only of mica waste ground to fine powder. Many bronzes are coloured by aniline dyes, which is accomplished by adding a solution of the dye in strong alcohol to the finely ground powder, and grinding intimately together. Only dilute solutions of dyes should be used, otherwise a uniform mixing of the mass can only be obtained by very protracted grinding.

Utilization of Copper-Wire Waste.—The so-called "leonische" wire is made from the finest and purest copper. Copper, cement, silver, and gold wire is made. The first has no coating; cement wire is coated with brass by exposing the copper rods, in a furnace, to zinc vapours. The silver wire has a coating of pure silver, and gold wire a layer of gold over the silver. Flattened wire is called ribbon wire or tinsel. When these wires are heated, the coating disappears; it sinks into the surface, and the wire then has the appearance of oxidized copper. When this wire is brought into glass tubes, and reduced in a current of hydrogen, it exhibits the finest copper colour. The waste of fine silver wire or ribbon wire may be advantageously used, according to E. Ebermayer, in organic analysis. This fine waste is very soft, fills the tubes completely, and easily transmits the current of gas. Cement wire naturally cannot be used on account of the zinc; only silver wire should be employed. The stouter wires, discoloured silver tinsel, and lump silver may be used to produce sulphur dioxide, after which the silver can be regained.

Utilization of the Residues of Galvanic Batteries.—The copper is first separated from the zinc solution by suspending scrap zinc in the liquid. The clear, colourless filtered liquid is then precipitated with milk of lime, when a useful zinc white of fair covering power, containing gypsum, is produced. It is particularly applicable as a water-colour in printing wall-papers, and in distemping. The zinc solution may also be boiled with a definite quantity of common salt, when there are obtained good Glauber's salt, suitable for use in glassworks, where a small quantity of zinc is not harmful, and zinc chloride, which can be used for impregnating timber and sleepers, also for producing artificial marble and a good lime cement. The zinc solution, on evaporation and strong ignition, evolves sulphur dioxide, which may be used for bleaching; hard zinc oxide is left, which is admirably suited for polishing purposes.

The copper solution is always too weak to be worked up for copper salt, therefore it is best to precipitate the copper with zinc, and obtain it in the finely divided state. In order to obtain solid copper, the copper mud and granules are collected, boiled twice with pure water, mixed with charcoal, 5 per cent of soda, and 1 per cent of borax, and fused to a regulus in a strong charcoal fire.

In order to obtain metallic zinc from the zinc solutions, the latter are evaporated to dryness with 10 per cent of powdered coal, and the residue calcined in horizontal retorts; the process is then the same as in zinc-works, i.e. the metal is distilled.

Recovery of Waste Nickel.—The following method is used in order to recover the waste of rolled or cast nickel anodes, and also the nickel sand, which gradually collects at the bottom of the cells: The waste nickel is repeatedly washed with clean, hot water, and then boiled in dilute sulphuric acid (1 vol. of acid to 4 vols. of water), until pure water, poured on the nickel, is no longer rendered turbid. The nickel scrap or sand is then thoroughly dried and treated with strong nitric acid. In this operation care has to be

used to prevent the solution from boiling over, for which purpose large porcelain vessels are used. If the solution begins to crystallize, pure water is added, and the mixture heated. The nitric acid solution of nickel must contain as little free acid as possible. The nickel nitrate is dissolved in hot distilled water, and the solution neutralized with pure caustic potash, which is cautiously added, a little at a time; the mixture is then carefully filtered. The nickel bath obtained in this manner acts directly on all metals, producing a hard silver-white deposit of nickel.

CHAPTER L.

TINPLATE WASTE.

Utilization of Waste Tinplate.—A. Ott, of New York, has obtained an English patent for utilizing waste tinplate.¹ The tin is recovered from the tinplate by means of a mixture of acids, which also dissolve lead contained in the coating on lower qualities of tinplate. From this solution the lead is precipitated by sulphuric acid and then the tin by means of sheet zinc; the tin is washed with water and melted. The acids also dissolve about 5 per cent of iron; for every two parts of tin about one part of zinc is dissolved; the liquid obtained, therefore, consists of a mixture of iron and zinc salts. It can be used for saturating wood, as a disinfectant, and also in the preparation of certain painters' colours. The iron, freed from tin, is washed in water, then in weak alkali, and, finally, again in water. It is sold to iron-works, where it is utilized in the puddling process.

The tinplate waste is brought into a perforated copper cylinder, which is brought by a crane to a series of vats placed in a semicircle round it. Each vat is provided with bearings for the axle of the cylinder, which is then rotated by mechanical power. The cylinder is 1·8 metre (71 ins.) long, 1·95 metre (78 ins.) in diameter; the body is made of sheet copper, 3 mm. (0·12 in.) thick, whilst the ends are 7 mm. (0·28 in.) thick; the body is perforated with holes 9½ mm. (0·38 in.) in diameter, and 50 mm. (2 ins.) apart, it is bound round with copper rods 10 mm. (0·4 in.) in diameter. A door with two flaps serves for the introduction and removal of the tinplate. This drum is brought in succession into each

¹ "Deutsche Industrie-Zeit."

of the four vats mentioned above, of which the first is the acid bath, the second is a slight alkaline bath, the third water, and the fourth again an alkaline bath. The four vats are of equal size; they are made of fir, 64 mm. (2.5 ins.) thick, are 1.3 metre (52 ins.) deep, 2.2 metres (86 ins.) long, and 1.9 metre (75 ins.) wide. The bearings for the drum are so placed in each vat that it is only half immersed. The first vat, which contains the acid bath, is lined with sheets of glass, cemented together with a mixture of sulphur and steatite. The charge for the cylinder is 430 kilos (967 lb.), and the duration of the operation, including emptying the drum, seventy-one minutes. For 1000 kilos of tinplate, 242 kilos of hydrochloric acid and 7 kilos of nitric acid are required on the average. The nitric acid is added to the hydrochloric acid when the latter is almost exhausted. At the commencement of the process, the acid vessel is two-thirds filled with hydrochloric acid of 20° B. After complete saturation, the acid is evaporated in copper pans to one-third of its volume, any lead which may be present precipitated by sulphuric acid, the clear solution drawn off into a large wooden tub after the lead sulphate has settled, and, after dilution with double its volume of water, the tin precipitated by zinc; 32.6 parts of zinc are required to 58 parts of tin.

According to Ott, the process of Seely¹ is much used in Switzerland, and with great success. The apparatus employed is a cylinder of boiler-plate, the bottom and top of which can be removed, but during use both are closed by glycerine lutes. A pipe enters the upper part of the cylinder, also through a glycerine lute. A delivery pipe leads from the lowest point of the bottom. In the lower part of the cylinder there is a perforated double bottom, which can be placed parallel with the bottom, or turned vertically down. The tinplate is heaped up on the false bottom, the bottom and the cover attached, and then chlorine gas introduced through the delivery-pipe. The reaction commences at once, and continues for a longer or shorter time according to the quantity of the

¹ "Muster-Zeit."

tin scrap; about five to six hours are required to remove the tin from 10 cwt. The resulting gaseous tin chloride may be passed directly into water; it is quite free from iron. To empty the apparatus, the bottom is removed, and then the false bottom, with the remains of the tinplate, allowed to fall down. The average quantity of tin contained in waste tinplate is $\frac{1}{2}$ per cent, thus, from 1000 lb., 11 lb. of anhydrous stannic chloride and 989 lb. of iron are obtained, for which 7 lb. of chlorine are sufficient.

Another method for utilizing copper and tinplate waste consists of the following process:¹ The waste tinned iron is introduced into copper solutions, in which the copper is present as chloride or sulphate; if this is not the case, sodium chloride and sulphate are added. The tin is loosened and precipitated as hydrate, the bared iron then precipitates the copper from solution. The stannic hydroxide is removed before the reducing action of the iron commences.

Noteworthy and very practical observations in regard to the treatment of waste tinplate have been made by C. Künzel of Blasewitz, near Dresden.² The purchase of tinplate waste requires a certain amount of caution. The thinner the tinplate, the more tin it contains. French tinplate contains more tin than English. Very frequently, however, a mixture of tin and lead is used for tinning iron; if the lead exceeds 10 per cent of the tin, the material should not be bought; such tinplate must always be separately treated, since it offers great difficulties in the process. Lacquered tinplate is also to be avoided since the lacquer is not thoroughly attacked by boiling in dilute acid; it is therefore necessary to destroy it by a gentle preliminary heating, which causes the yield of tin to be somewhat lower. In delivery contracts with dealers the quality of the tinplate must be exactly stipulated. Since it is impossible to stipulate for a certain proportion of tin in buying tinplate waste, the material must be inspected and a price offered according to the thickness of the plate—the thinner the more valuable—with the arrangement that, if

¹ "Dingler's Journ.," 219, p. 96.

² "Berg- und Hüttenmännische Zeit."

iron coated with lead or zinc is added, the delivery will be rejected. When old barrels or packing-cases are to be had cheap, the waste is stamped down in them for transport; otherwise, compressed packages are made, weighing 1-2 cwt., by stamping the waste into a strong rectangular wooden box, somewhat wider at the top than the bottom, by means of a strong rammer, and then binding the packages together by means of two crossed iron wires or old hoop iron. In treating these compressed packages of waste tinplate, it is necessary to loosen them as far as possible, so that no two surfaces of tin may be in such close contact that the acid cannot penetrate between them. This is best done at first with a large three or four-pronged fork, and afterwards by loosening and bending by hand.

To dissolve the tin from the waste tinplate, Künzel employs a boiling mixture of one part of strong nitric acid and ten parts of strong hydrochloric acid diluted with so much water that the liquid remains about four inches deep over the waste when the boiling is finished. The liquid is contained in wood or brick vats lined inside with a mixture of two parts of sand and one part of sulphur, applied hot. A pipe of vulcanized rubber reaches to the bottom of one of these vessels, which should not have a less capacity than 1 cub. metre (35.3 cub. ft.); the vulcanized pipe is fastened above to a copper pipe, which is in communication with a steam generator.

The empty vat is almost completely filled with the loosened tinplate waste, then the acid mixture is added after it has been diluted to such an extent that it covers about four-fifths of the tinplate. Steam is now allowed to enter in order to heat the solution to boiling; the introduction of steam is continued, with the valve only so far opened that the liquid just boils, until the upper parts of the tinplate are entirely freed from tin and the evolution of hydrogen has almost stopped. On an average, the boiling lasts thirty to forty-five minutes. The solution, which contains all the tin and a certain quantity of ferric chloride, is run off whilst

still hot, by opening a tap at the bottom of the vessel, into a tank, where the greater part of the lead chloride separates on cooling. On the average, for 1000 kilos (1 ton) of tinplate containing $\frac{1}{2}$ per cent of tin, there are required 60 kilos (120 lb.) of hydrochloric acid and 30 kilos (66 lb.) of nitric acid, which are diluted with about 3.5-4 cub. metres (123-140 cub. ft.) of water or wash waters.

The residual iron is washed with water in the dissolving tank, the washings being used to dilute the acid for the next operation. The iron is then lifted out by means of forks, and as quickly as possible stamped into bundles. It is dangerous to keep this iron waste piled up loosely in large heaps since it readily oxidizes, and may become red hot. For the treatment of 3000 kilos (3 tons) of waste tinplate per day of twelve hours, six or seven dissolving tanks are required, each of 3 cub. metres (106 cub. ft.) capacity, otherwise an excessive amount of labour is requisite.

The cooled solution drawn off from the tin plate is brought into large wooden tubs or stone tanks filled with old zinc plates, old zinc roofing sheets, etc., by which the tin is precipitated, together with any lead present in the liquid. The precipitation must take place without any noteworthy evolution of gas; if any effervescence occurs, the solution is too acid and zinc is wasted. The filtered solution is tested by slightly acidifying, and passing in sulphuretted hydrogen, to see if all the tin is precipitated. The precipitation requires two hours at the most. A tap at the bottom of the tub is then opened, and the clear solution, which it is impracticable to utilize further, run off through a strainer of sailcloth. The zinc remaining in the tub is then gently shaken to remove the deposited spongy tin; the tub is again filled with the solution obtained by boiling the tinplate, and the process thus continued, with occasional replacement of the zinc as it dissolves, until the tub is filled to the extent of one-third to a half with spongy tin.

The spongy tin is removed from the tub and washed through a metal sieve with a mesh of 3-4 sq. mm. into a sail-

cloth strainer by means of a stream of water. Small undissolved pieces of zinc remain on the sieve and are returned to the precipitating tub. Solder is also caught by the sieve; it is melted and sold as soft solder. The spongy tin which has passed through the sieve is washed with water on the linen filter so long as the washings contain iron. It is then squeezed in linen bags under a hydraulic or screw press in order to remove as much water as possible. The spongy tin so obtained is now converted into tin crystals (stannous chloride); it is desirable to dissolve it in hydrochloric acid immediately after it has been pressed. The manufacture of tin crystals is sufficiently well known; Künzel therefore gives further only the treatment of the insoluble residue obtained in dissolving the spongy tin. This consists principally of lead chloride and stannic oxide; Künzel has successfully treated it by mixing with about two volumes of common small coal, and heating it to a red heat in a small Belgian zinc furnace, with six retorts set in two series at a considerable inclination to the front. If sufficient lead chloride is not present, it is added from that obtained in the cooling-tanks from the tin solution. All the tin present then passes into the receiver, as stannic chloride, whilst metallic lead is formed at the same time; the latter partly runs into the receiver, and is partly recovered in grains by washing the residue in the retort.

In regard to the treatment of the residue of iron, Künzel is of opinion that, with a daily treatment of a small quantity of waste tinsplate, and where sulphuric acid is to be obtained at a low price, the waste iron may be profitably converted into green vitriol.

Künzel obtained a good product by making the waste iron up into bundles of about 5 kilos (11 lb.) and introducing it into the puddling furnace at the moment when the iron is in the most spongy condition, the quantity being 10-20 parts to 100 parts of pig-iron. An excellent white cast-iron was obtained by melting 2 parts of the waste iron with 5 parts of grey cast-iron turnings in the cupola furnace.

W. D. Walbridge proposes to immerse waste tinfoil as the positive pole in a bath containing 3 kilos of caustic soda, 1 kilo of sodium nitrate, and 7 litres of water; or 3 kilos of caustic potash, 1 kilo of potassium nitrate, and 7 litres of water; or, finally, 0.2 kilo of caustic potash, 2 kilos of common salt, and 7 litres of water, whilst the iron vessel forms the negative pole. The inventor has obtained a patent for the process.

E. Roussett recommended the following method: In the first place, the tin must be heated in an oxidizing flame, which oxidizes all the free tin, and also that combined with iron. The tinfoil is now covered with a brown, brittle crust, the upper layer of which consists of stannic oxide, and the lower of the magnetic oxide of iron; it is then squeezed between grooved rollers in order to remove the oxides, which are sieved and collected. The residual iron gives a good wrought- or cast-iron, but is said to be especially suitable for precipitating copper. The stannic oxide, although mixed with the iron oxide, can easily be reduced to metallic tin by the usual methods; the metal obtained is free from sulphur and arsenic.

Tinfoil Waste.—J. Rosenthal, Berlin, in a patent (Ger. Pat. 288,533, Nov. 12, 1913) claims the use of concentrated sulphur oxy acids for stripping the tin from tinfoil; these remove the tin, at the same time rendering the iron passive. Oxidizing gases are excluded during the operation.

CHAPTER II.

CALAMINE SLIMES.

Utilization of the Residues.—Prof. Schwarz proposes extraction with hydrochloric acid, as a means for obtaining zinc from calamine slime.¹ When the slightly roasted calamine is mixed with exactly the proper quantity of very dilute sulphuric acid required to saturate the zinc oxide the latter is largely dissolved. When a calamine slime containing 9.5 per cent of zinc oxide is lightly roasted, and then mixed with the quantity of 2½ per cent hydrochloric acid equivalent to the zinc oxide, 5.6 per cent of zinc oxide is dissolved. When the residue was again treated, the percentage of zinc left was reduced to 1.5, so that altogether 8.0 per cent was dissolved.

For 40 parts, by weight, of zinc oxide, or 32 of zinc, 36 parts of anhydrous hydrochloric acid are required, or about 120 parts of strong hydrochloric acid of 30 per cent strength. Thus 100 kilos of zinc require 375 kilos of hydrochloric acid. If the crude hydrochloric acid at the works costs 2.5 marks per 100 kilos (about 1s. 3d. per cwt.), 100 kilos of zinc would require acid worth 9.37 marks, which, with zinc at a price of 48 marks (24s. per cwt.), would leave a possibility of profit. There would be in addition the cost of precipitating by milk of lime, drying, and reducing to metallic zinc, although the latter, in view of the fine state of division of the precipitated zinc oxide, would take place readily and with a small consumption of fuel.

Recovery of Zinc—No. 9009 of 1915.—F. W. Highfield, of Whitchurch Mill, Whitchurch-on-Thames, claims: (1) In apparatus for use in the recovery of zinc other than that

¹ "Dingler's Journ.," 218, p. 212.

claimed in claiming-clause No. 2 of my prior Letters Patent No. 6865 of 1914, namely, other than that where in a bed of electrically heated carbon is supported upon a grate above a chamber to receive the reduced zinc in combination with means to feed zinc oxide or blue powder on to the glowing surface of the said carbon and with a cooling chamber containing a neutral or reducing atmosphere in direct closed communication with the aforesaid chamber, a wall or septum to afford a condensation surface for zinc that is porous to carbon monoxide or hydrogen at the working temperature, but is impervious to liquid zinc and the material of which is not attacked at that temperature by zinc, by carbon monoxide or by hydrogen with or without means provided for the purpose of maintaining the temperature of the wall or septum at the required value. (2) The combination with one or more zinc retorts of a condensing chamber having a wall or part of a wall formed of material that is porous to carbon monoxide at the working temperature of the condenser and is not attacked at that temperature by zinc or by carbon monoxide with or without means provided to maintain the temperature of the said wall or part of a wall at a temperature higher than that at which it would be maintained by the vapours introduced into the condenser. (3) A wall or septum according to claiming-clause No. 1 or No. 2 made of porous fire-clay or of carbon or of porous porcelain.

See also "Proceedings of the Paint and Varnish Society," London, February, 1918, paper by W. F. Reid.

CHAPTER LII.

WASTE IRON AND IRON SLAGS.

Utilization of Scrap Iron.—From manufacturing operations and also from kitchen refuse very large quantities of scrap iron are obtained. This is collected by dealers, the greater part of it being sent back to the iron and steel furnaces to be re-melted.

In the treatment of pyrites containing 3 or 4 per cent of copper, the sulphur is first utilized in the manufacture of sulphuric acid, the burnt pyrites is then roasted in a furnace with common salt at a regulated temperature, whereby cupric chloride is formed; the cupric chloride is then dissolved out with water and the solution run into large vats containing a mass of scrap iron. Here the copper is deposited in a fairly pure state and after drying is ready for smelting.

IRON SLAGS.

Slag Wool.—In 1875 a loose substance somewhat similar to natural cotton was brought into the market by the owners of several ironworks—by K. Marien, of Zwickau, and G. Marien, of Osnabruck. The substance differed from cotton in consisting of straight (not curled) fibres, being shining and somewhat less soft to the touch. The new product was produced by forcing steam into a jet of fluid slag.

Slag wool has hitherto been produced only from blast-furnace slag. According to Schliephake,¹ it is best made by blowing with a current of high-pressure steam, whilst the slag is conveniently drawn off from the furnace through the Lürmaun slag mould. It is a considerable drawback to the

¹ "Polyt. Journ."
(307)

operation that the many fine fibres floating in the air seriously injure the workmen.

Slag wool is utilized in accordance with its properties, of which the most important is its very low conductivity for heat. In covering steam-pipes, the slag wool is laid on the pipes in pieces of about 1000 sq. cm. (160 sq. ins.) with a firm pressure from the hand, without beating. A thickness of 8 cm. (3-4 ins.) suffices for most pipes. The slag wool, compressed to this extent, is bound round with twine or wire, so that it adheres to the protected pipe. After one or two yards of a steam-pipe have been covered in this manner, the whole is sewn up in coarse sacking, which may then be coated with tar, to prevent the penetration of water; wet slag wool is a better conductor than dry, which is also the case with other poor conductors. For 1 sq. metre of surface to be protected in this manner, about 4 kilos of slag wool are required (9 lb. per sq. yd.). A steam-pipe or cylinder so covered is hardly perceptibly warm on the outer surface.

From another practical source it has been stated that the covering of sacking is little used, since it is soon destroyed by the action of light and heat, even when tarred.

It is recommended, in covering pipes with slag wool, to make use of a cylinder of sheet iron, the diameter of which is 150 mm. (6 ins.) more than the external diameter of the pipe. The sheet-iron cylinder is 300-400 mm. long (1-1½ ft.), and is divided lengthways into two halves, which are bound together by splints or similar means. Each half has a handle in the middle. This sheet-iron cylinder is placed round the pipe in such a position that one end is closed by a flange; the slag wool is then forced into the space between pipe and cylinder, which is about 75 mm. (3 ins.) wide. When the interspace is filled, during which operation too hard stamping is avoided, the sheet-iron cylinder is moved forward with a gentle rotatory motion to-and-fro by means of the handles, and the covering of slag wool wrapped with wire as it becomes exposed. The forward movement of the cylinder and the wrapping with wire must keep pace. The

whole surface of the slag wool is moistened with tar, and then covered with a coating of cement about 5 mm. (0·2 in.) thick. About 10-12 kilos of slag wool are required to cover a surface of 1 sq. metre to a thickness of 75 mm.

The fireproof nature of slag wool, combined with its low conductivity for heat, makes it a very suitable substance for the lining of fireproof safes. Wolpert, of Kaiserslautern, first drew attention to its use as a filling material for floors and wainscoting in buildings. "Slag wool," he says, "at present usually contains calcium sulphide, which is decomposed into calcium carbonate and sulphuretted hydrogen by the action of the carbonic acid in the air and the water which obtains admittance in washing the wainscot. Sulphuretted hydrogen is known (when breathed in quantity) to be a poisonous gas; accordingly slag wool for such purposes must be examined for calcium sulphide. If vinegar be poured on slag wool moistened with water, the well-known smell of sulphuretted hydrogen—that of rotten eggs—is perceived, if the wool really contains calcium sulphide."

But these opinions against the use of slag wool as a filling for floors, etc., go too far; according to Wolpert himself¹ the normal quantities of water and carbonic acid in the air can barely produce a perceptible evolution of sulphuretted hydrogen. Apart from its very bad conducting powers, the layer of slag wool has also great permanence, can withstand a considerable temperature, and is not liable to decay through the action of moisture or gases.

Slag Stones. Slag Bricks.—The production of slag stones dates from 1860. At Osnabruck, at that period, the fluid slags were allowed to fall, like molten lead in the shot-towers, from a height of about 8 ft. into water, where it formed large bean-shaped lumps, which were used, instead of road-metal, as ballast on railways. The same thing had been done for a long time in England, where the slag was broken with a Blake's stone-crusher, and used for macadam. In particular, the slags obtained in the Bessemer process, when

¹"Polyt. Zeits."

the pig iron was made from spathic iron-stone, are said to be suitable for producing artificial paving-stones, in consequence of the lime they contain.

More recently the best method for this utilization of blast-furnace slags has been attained by granulating. C. Paschan has published a communication on this subject in the "Notizblätte des Vereines für Fabrikation von Ziegeln".

The product, the so-called slag gravel, can only be used with the best success as the embedding material for railway sleepers, but it produces, when mixed with lime in the proper manner, the material for an excellent slag building-stone and slag mortar.

The preparation of slag gravel by granulation simply consists in allowing the fluid slag to flow into water, where, by the sudden cooling, purified slags harden to a pumice-like gravel and less purified slags to coarse grains.

Slag-stone is in no way inferior to good brick, which it surpasses in fineness of colour and porosity. Although at first friable, it rapidly hardens in the air. This hardening continues for a long time, even after the stone is used, and, since the mortar is also mixed with slag gravel, the stones are completely bound, so that after several years a wall consists no longer of separate stones, but of one uniform mass.

At the ironworks of Buderus, at Gollar, near Giessen, building-stone is made from blast-furnace slag in the following manner: ¹ A portion of the hot fluid slag from the blast furnaces is cast in large round iron vessels standing on trucks. These go to the portion of the works where the compressed stone is made, and after cooling are emptied. The blocks of slag gradually fall on contact with air to a fine bluish-grey meal—slag meal. The greater part of the hot fluid slag, however, runs into a channel, in which cold water passes in rapid motion. The slag is thus granulated; the sand produced is mechanically scooped out, brought into the wagons of a wire-rope tramway, which take it to the working place, where they are automatically emptied. Foundry slags

¹ Report by the engineer Alberte, "Gewerbebl. f.," Hessen, 1893.

have been found to be the best, as they produce the lightest stone. In producing the compressed stone, the slag sand is mixed with the above-mentioned slag meal and milk of lime in the following manner: A mixture of 2 parts of sand and 1 part of meal is moistened with milk of lime, the moist mass is shovelled into presses and moulded into stones. The automatic steam lever presses of Bernhardt's Son G. F. Draenert of Eilenburg, have been found to work especially well.

The stones are made in two sizes—the small size 25 by 12 by 6.5 cm. (10 by 5 by 2.6 ins.), and the large size 25 by 12 by 10 cm. (10 by 5 by 4 ins.). They have a bluish-grey colour and are fairly porous. The two horizontal faces are somewhat hollowed out, in order to diminish the weight of the stone and to admit a larger quantity of mortar with apparently narrow joints. The weight of one stone, air-dried, is about 3.3 kilos (about 7.4 lb.). They are crushed by a load of 70 kilos per sq. cm. (1000 lb. per sq. in.). They take up a large quantity of water, and have not a great resistance to the action of fire—a red heat. The stones are not burnt but only dried in the air.

The slag sand by itself is a very useful addition to mortar. A useful rough plaster is obtained from a mixture of 3 parts of slag sand, 2 parts of slag meal, and 2 parts of clay, whilst for fine plaster a mixture of 1 part of slag meal, 2 parts of white lime, 4 parts of river sand, quarried sand or slag sand, is recommended. The sand for this purpose must be finely sieved.

F. Kirmmeier, of Speyer-on-Rhine, prepares moulded stones from blast-furnace slag.¹ The slag is cast in long rectangular blocks notched at suitable intervals, so that when the separate blocks are broken off, stones with granular crystalline ends may be obtained. The moulds used in this process are made up of separate walls with an open side, through which the slag can enter. On the under surface of the cover, on the bottom and on the sides, are triangular

¹ German Patent, 1895.

ribs, which facilitate the division of the long blocks into separate stones after cooling.

Great improvements have been made in the manufacture of slag bricks, to improvements in brick presses and to the use of dry disintegrated lime, which is added to the slag sand (containing as much as 40 per cent of water) as required. Although the granulated slags, on account of the soluble silicic acid they contain, would harden if pressed or stamped alone, yet they do so more rapidly if lime is added. The stone hardens through the formation of calcium carbonate, in a similar way to ordinary mortar, and especially through the formation of solid compounds between the soluble silica, the slag, and the added lime.

Slag bricks are made in the following manner: The hot fluid slag is conducted into a suitable cast-iron channel, through which a sufficient stream of cold water is flowing. The slag is chilled and falls partially into sharp sand, partially into very brittle lumps, the latter being readily broken by a slight pressure. The slag sand passes into catch boxes, from which it is taken by baskets with perforated sides and conveyed to the brick-moulding works. It is mixed with the milk of lime as follows: The slag sand is shovelled into the stirring-machine, whilst the proper quantity of milk of lime at 8-10° B. is run in. The mixture is then moulded in the brick press. The slag sand, mixed with lime, passes into a holder from which the necessary quantity is taken by two pistons into the press. The bricks are ejected from the press, taken by labourers, and placed in a tram wagon. They dry in eight days. Dark slags have not been found as suitable as pale slags for the production of bricks.

The slag sand is removed from the water basin after granulation by means of a strong scoop-wheel, which is constructed as follows: The scoops are fastened by screws between two large cast-iron rings, which are hung on two friction rollers with a common axis. The latter is driven by gearing from a small steam-engine built on to one of the four cast-iron pillars. The external periphery of the friction

rollers works on the inner periphery of the rings and turns the scoop-wheel, which is prevented from oscillating by two guide rollers at the side. The internal diameter of the rings is such that a line of rails goes through the scoop-wheel, so that a wagon may be pushed in from one side and out at the other when full. The two cast-iron rings, together with the twenty-four scoops, weigh about 90 cwt. The weight of slag to be lifted on at once is about 6 cwt. at most. The apparatus makes a revolution in about five minutes with the engine running at eighty revolutions per minute, so that the arrangement can load 72 cwt. of slag per hour. The rings, and also the columns which support them, are cast at the furnace, and need no further working. The feet of the columns are so wide as to offer a sufficient surface for the foundation, and are therefore built on the masonry of the water basin. The spindles of the steel driving shaft, upon which hangs the whole weight of the scoop, run in ball bearings, which are carried by a wedge in a fork and are adjustable. The fork hangs between the U-pieces which rest on the columns and form the framework of the machine.

Blast-furnace Slags as Paving-stone.—It has been found that blast-furnace slags make a good paving-stone. The Altona paving-stone, made from iron slags, consists of powdered slag, mixed with clay or loam as a binding agent, compressed and burnt to vitrification.

The paving-stones are laid in a bed of sand only 8 cm. deep (3·2 ins.), stamped down with an ordinary wooden rammer, and the joints then filled with sand and water. The method of laying may thus be called easy and rapid. These stones do not wear hollow like sand-stone, or smooth like granite slabs; they can readily be taken up and laid aside without suffering any injury, which is important when excavations are made for gas and water-pipes.

The price of these slag stones varies, according to the state of the market, between 225 and 280 marks per 1000. To this is to be added the cost of discharging, loading, and

transporting to the destination, which may be taken at 15 marks per 1000.

Glass from Blast-furnace Slags.—According to a patent of Basley Britton, at the ironworks of Chesland & Fisher at Wellingborough, the fluid blast-furnace slags direct from the furnace are worked up into glass, for which purpose they are conducted into a tank holding three-quarters of a ton, and there mixed with other suitable materials. The glass is said to be quite transparent, and extremely soft or plastic; it resists acids, is readily cut by the diamond, and is quite suitable for rough sheets for roofs, skylights, etc. It is cheaply obtained, since the heat contained in the slags is also utilized in the process.

Salts from Blast-furnace Slags.—According to a French patent,¹ aluminium sulphate, gelatinous silica, and calcium chloride can be obtained from blast-furnace slag. The slag, in fine powder, is treated with hydrochloric acid in an acid-proof apparatus, the acid vapours evolved being condensed in a sand-stone receiver filled with water. The acid solution, containing dissolved silica, aluminium and calcium chlorides, is drawn off, diluted with water, the silica allowed to settle, the liquid decanted off, the alumina carefully precipitated by pure calcium carbonate, the precipitate washed, dried, and converted into aluminium sulphate by boiling sulphuric acid. The gelatinous precipitate of silica is purified by washing, and the calcium chloride solution, remaining after precipitation of the alumina, is evaporated.

Slag Cement.—Ordinary blast-furnace slag contains as its principal constituents silica, alumina, and lime, which are also the essential constituents of Portland cement, though they are present in the latter in different proportions.

The accumulation of enormous quantities of iron slag in the neighbourhood of blast-furnaces led to many attempts being made to utilize it. One of the first instances of the application of slag to industrial purposes was that at the Cleveland Slag Works where blast-furnace slag was con-

¹ Post's "Zeits. f. d. chem. Grossgew."

verted into a cement by grinding under edge-runners 70 per cent of slag sand, 15 per cent of common lime, and 15 per cent of oxide of iron (burnt iron pyrites or iron-stone). The relationship of iron slag to Portland cement will be seen by the following analysis :—

	Cleveland Iron Slag.	Portland Cement.	Slag Cement.
Lime	32.61	60.88	22.90
Silica	36.50	23.16	21.60
Alumina	22.95	7.68	19.85
Ferrous oxide	0.06	—	4.00
Ferric oxide	—	3.00	8.80
Manganous oxide	0.32	—	0.21
Magnesia	5.83	1.01	4.36
Potash	0.59	0.72	0.50
Soda	0.31	0.31	0.32
Sulphur	1.73	0.05	1.19
Sulphuric acid	—	2.60	1.54
Phosphoric acid	—	0.08	0.02
Carbonic acid	—	—	3.00
Water	—	0.77	12.00
	<hr/> 100.90	<hr/>	<hr/> 100.29
Deduct oxygen = sulphur	0.86		0.59
	<hr/> <u>100.04</u>	<hr/> <u>100.26</u>	<hr/> <u>99.70</u>

Manure from Slag.—In the manufacture of steel by the Bessemer and open-hearth processes the silicon contained in the iron and also from the furnace lining is oxidized to silicic acid which combines with whatever bases are present and also some of the iron to form slags, but the silica being in excess very little sulphur and phosphorus is oxidized, hence pig iron containing a percentage of these elements could not be used in steel-making. By the introduction of the “basic” process, i.e. one in which the lining is composed of magnesite, Thomas and Gilchrist were enabled to produce perfectly good steel from cast iron containing both phosphorus and sulphur, the same applying to the Bessemer process. In this case there is sufficient base present to combine with the acids as fast as they are formed, which results in the oxidation of the whole of the silicon, phosphorus, and sulphur.

The slag produced by the Thomas-Gilchrist process floats on the surface of the steel, from which it is removed before the metal is tapped. It was found to be quite different to ordinary slag as it contained a fairly high percentage of phosphates. The utilization of this slag as a manure was not long in coming, and at the present time large quantities of it are used for this purpose. For the purpose of manure it is ground in disintegrators and then under edge-runners. The slag contains 45-60 per cent of lime and 10-20 per cent of phosphoric acid.

Iron from Burnt Pyrites.—According to P. W. Hofmann¹ burnt pyrites is treated in the following manner in order to obtain the iron: It is methodically extracted with water at about 40° C.; one equivalent of sodium chloride is added for each equivalent of sulphuric acid contained in the liquor, the Glauber's salt removed by cooling, and the mother liquor evaporated to 54° B. in order to obtain zinc chloride. The burnt pyrites is then removed from the washing-boxes, left for some days in the air to dry, and then sieved to separate the sulphurous material from that free from sulphur.

According to J. Cahen,² the burnt pyrites of vitriol works is well mixed with tar, turf, and lime-stone, the mixture made into lumps of suitable size, and treated in a blast-furnace. The iron obtained is said to be almost free from the ordinary impurities of pig iron; any sulphur still present in the burnt pyrites combines with the lime, and the turf apparently effects the formation of volatile phosphuretted hydrogen.

See "The Oil and Colour Trades Journal," "Potash from Blast Furnace Dust," pp. 223, 548, 1401, vol. I, 1918.

¹ "Dingler's Journ.," 215, p. 239.

² "Ber. d. deutschen chem. Gesellsch."

CHAPTER LIII.

BY-PRODUCTS OF THE MANUFACTURE OF MINERAL WATERS.

Utilization of the Magnesite Residues.—Magnesium sulphate, the by-product of the manufacture, consists of water (of crystallization), 51·2 per cent ; sulphuric acid, 32·1 per cent ; and magnesia, 16·7 per cent. The two last constituents are indispensable plant-foods ; the magnesia, in particular, occurs in the seeds of cultivated plants—in grain, leguminous plants, etc.—in relative'y large quantity. In the condition in which it is produced by mineral waterworks, magnesium sulphate contains 6·7 per cent of impurity, and is therefore, according to Prof. v. d. Goltz, almost equal to the pure salt in value for agricultural purposes. Manuring plants with magnesia, i.e. with sulphate of magnesia, has repeatedly been found successful. It would be advisable to mix the salt with an equal quantity of loose earth, and then to spread the mixture over the young plants, or over fields just beginning to sprout. For leguminous plants 0·5-0·75 cwt. of magnesium sulphate is applied per acre, 1-1·5 cwt. for clover and pasture land. Strewing magnesium sulphate over stable manure or dung-heaps is also strongly recommended.

Luhmann advises the preparation of *pure magnesium sulphate from this by-product*.¹ Since the salt is not contaminated with other soluble salts, but only with small quantities of insoluble residue and finely divided calcium sulphate (gypsum), a clear concentrated solution of pure magnesium sulphate can be obtained by systematic lixiviation. This process is conducted in a number of vats, the first of which is filled at the commencement with a strong solution of the magnesite residue in water. After the white precipitate of gypsum has settled

¹ "Die Kohlensäure," Vienna, Hartleben.

to the bottom, the clear liquid above is drawn off by a syphon, and brought into a larger collecting tank. Fresh water is added to the gypsum and stirred with it; then, after settling, the dilute, clear liquor is drawn off and brought into the second vat, where it is saturated with magnesium sulphate from a fresh portion of magnesite residue. In order to fill this vessel completely, a sufficient quantity of water is added in dissolving the residue. Water is again brought on to the precipitate in the first vat, and the mass stirred. After settling, the liquor of the second is transferred to the collecting vat, and the now very dilute liquid in the first to the second; whilst in the third vat a strong solution is made from the dilute liquor, water, and fresh magnesite residue. The process of lixiviation is thus continued, fresh vats being added until the first only contains pure water, and the Baumé hydrometer sinks to 0°. The strength of the liquors is estimated by means of this hydrometer; magnesium sulphate solution, which is saturated at 15° C., has a specific gravity of 1.299 = 16.5° B. When the hydrometer sinks to 0° in the first vessel, the water is drawn off, the gypsum mud removed, and a strong solution of magnesium sulphate made in it from a fresh portion of the residue and dilute liquor; this vessel is now to be regarded as the last of the series.

The united strong solutions of the salt are evaporated in an iron pan until a skin of salt forms on the surface, or until the hydrometer stands at 37°. After the dissolved iron has been precipitated by liver of sulphur, the fire is removed from under the pan and the liquor allowed to rest for some time until it has become clear; it is then drawn off by a syphon, filtered through a strainer, and brought into a cooler, where the salt separates in small crystals on cooling. As soon as the salt has formed a layer on the sides of the cooler about 3 cm. (1¼ in.) thick, the crystals are stirred up with a spatula, so that the crystals subsequently formed may not be too large or the mass of salt at the bottom too hard. After the mother liquor has been run off through the bung-hole of the cooler, and brought back into the pan, the

mass of crystals is piled up on a capacious drainer and finally dried on gratings in a drying-stove. The iron pan is then again filled with the cold saturated solution of magnesium sulphate from the lixiviating tanks, in order to prepare a fresh portion of the crystalline salt.

CHAPTER LIV.

INFUSORIAL EARTH.

Utilization in the Manufacture of Ultramarine.—The application in the manufacture of ultramarine was the first time infusorial earth was used in industry. In making ultramarine rich in silica, infusorial earth was added to pure clay, in place of quartz sand. It is certain that it has been much used for this purpose in recent times. Infusorial earth is a very *bad conductor* of heat; it is accordingly used for filling the insulating spaces of ice-cellars; similarly it is an excellent filling material for safes and ice-boxes. It is especially to be recommended for *cleaning glass plates* for photographic purposes. Even very greasy glass plates rapidly become clean when rubbed with infusorial earth moistened with water. Also, when it is required to use acids, alkalis, and solvents for cleaning purposes, they may, in a certain sense, be used in the solid form, i.e. mixed with infusorial earth, which is able to take up more than double its weight of liquid without becoming fluid. Infusorial earth is a very valuable material for *glass-making*, since it accelerates the formation of the glass by readily mixing, on account of its fine state of division, with the other materials. Similarly, infusorial earth is an excellent *grinding material* for hollow glassware.

In preparing water-glass, 74·5 parts of calcined soda are dissolved in five times the quantity of boiling water, 42·5 parts of slaked lime are added, and the mixture kept at the boil until a small portion of the liquid, when mixed with an acid, no longer effervesces. After the deposition of the chalk, the clear liquid is syphoned off, the chalk again boiled with water, the two liquids united and evaporated down to a

specific gravity of 1.15. To the boiling liquid 120 parts of finely powdered infusorial earth are gradually added; after this has dissolved, 3 litres of lime water are added. There is then produced a brown precipitate, which removes from the solution the organic matter derived from the infusorial earth. The liquid poured off from the precipitate, after it has been evaporated to a syrupy consistency, solidifies on cooling to a yellowish jelly, which dries completely in the air, and readily dissolves in hot water. 120 parts of infusorial earth produce 240-250 parts of a jelly, which contains 47 parts of anhydrous soda water-glass and 53 parts of water.

Infusorial earth finds a further application in the *manufacture of light bricks*; 24 parts of Lüneberg infusorial earth, with 1 part of fat clay, give a mass which works well. The infusorial earth, which has generally too little binding power, requires an addition of binding clay, with which the very fine earth can be mixed only by a very careful process of stirring together with water; also a temperature as high as that of the procelain kiln, which is rarely reached in a brick kiln, is required for burning.

Kieselguhr or fossil meal is also mixed with common clay and water and used as a non-conducting coating for boilers and steam pipes; for this purpose it is applied first in rough coats with the hand, then smoothed off with a trowel and in most cases covered with canvas which is stitched on and then painted with a mixture of chalk and sodium silicate solution.

CHAPTER LV.

MEERSCHAUM.

Utilization of Meerschaum Waste.—The dust and cuttings produced in making genuine meerschaum pipes are carefully collected and used to produce imitation meerschaum, which, however, is considerably inferior to the genuine in quality.

According to T. Urban,¹ the waste from genuine meerschaum is stamped in a barrel with water, the coarse mud brought into a mill, consisting of two stones, one lying close on the other, and here ground still finer. The paste is then rubbed by hand through a linen cloth stretched over the top of a tub. The fine material is now well boiled with linseed oil with the addition of alum. The linseed oil imparts to the imitation meerschaum a peculiar lustre similar to that of the real; the alum takes the place of a binding medium. When the boiling is finished, the meerschaum is brought into moulds and allowed to lie in the stove until the adherent water has completely evaporated and the mass has acquired a consistency of about that of soap. When this stage is reached, it is easy to force it into any required mould or to shape it with the knife.

When the shape of the pipes is roughly produced, the shaping is completed on the lathe. The pipes are then dried in a stove at 75-87° C., and subsequently boiled in melted suet. After cooling, they are rubbed with grass (*equisetum*). After rubbing, the best qualities are dipped in boiling spermaceti or wax, which causes them to colour more quickly when used, and at the same time gives the meerschaum a better polish and greater hardness. Meerschaum pipes burnt black inside and out are in equal

¹ "Dresd. Gewerbevereins-Zeit."

demand with the white pipes; they are distinguished by a very fine polish. The blackening is obtained by placing the white pipes for fifteen to thirty minutes in boiling linseed oil, and then holding them over burning pine sawdust until they are coloured black or dark, after which they receive the real polish.

The red meerschaum pipe, or oil pipe, is a lower quality, which is obtained by first boiling the cut pipe in fat, then turning, polishing, and finally again boiling. The red colour is produced by adding dragon's blood to the linseed oil; dragon's blood being added more or less according to whether the colour is to be dark or pale. Carmine, gamboge, and alkanet are also used as colouring matters.

The imitation pipes—made from waste meerschaum—are also carved. The carving being done in the half-boiled state, and the pipe finally again boiled.

J. S. Hyatt, of Paris, has discovered a process for the *preparation of a plastic substance from meerschaum waste, nitrocellulose, and camphor.*¹ In making certain articles, the shape and size of which considerably exceed those of the crude lumps of meerschaum, it is evident that both real meerschaum and the waste may be used, since the cost of treating and moulding the composition for this purpose is considerably less than that of the system now used—cutting the articles out of the solid. The process used is as follows: In the first place, the meerschaum waste is converted into a fine powder, next a solution is made, containing 5 parts by weight of nitrocellulose and 3.5 parts of camphor, by adding a quantity of ether (about 1 part) and alcohol (about 3 parts), or other liquids in which nitrocellulose dissolves, sufficiently to produce a viscid mass. The proportions of the four constituents here given have yielded excellent results in practice. They are not, however, to be regarded as absolute, and may be varied within certain limits according to the nature of the raw material and of the object to be produced.

Powdered meerschaum is added to the above solution in

¹ "Ackermann's illustr. Gewb.-Zeit."

the proportion of about 100 parts of meerschaum to 5 parts of the dissolved nitrocellulose. The whole is then thoroughly mixed in any desired manner, and the excess of solvent allowed to evaporate by natural or artificial means. The mass is next thoroughly powdered; the powder is the substance actually used in making a large number of articles. For this purpose it is filled into moulds made of metal or other material, and heated to a temperature of 100-120° C.

CHAPTER LVI.

MICA WASTE.

THE muscovite or potash mica which occurs in the form of fine glistening scales as one of the constituents of ordinary granite sometimes occurs, in the United States, Canada, etc., in very large crystals up to 1 or 2 ft. in diameter. These crystals can be split up very readily into extremely thin sheets which are elastic, practically fireproof, and non-conductors of electricity, hence they have come into use for lamp-glasses and especially for electrical apparatus. In cutting up these sheets, however, there is a considerable amount of small stuff formed which had to be thrown aside as it was of no use for that particular purpose.

During the last few years, however, uses have been found for this waste. It is ground up and graded into particles of various degrees of fineness by passing it through reels covered with wire gauze. The finer material is put into lubricants, soap, paint, etc., but the larger particles in very thin flakes are used for decorative purposes, for instance, in the preparation of the "satin" wall papers; it is also dyed with aniline dyes and used instead of metallic bronze powders, the range of colours being very much greater. By means of these artificial bronze powders some of the finest wall paper decorations in existence are prepared. The powders are very much lighter in weight, the colours purer and brighter than those of metallic bronzes, at the same time there is no tendency to tarnish by exposure to the air or in contact with varnish.

CHAPTER LVII.

SLATE WASTE.

Utilization of Waste Slate.—At the slate quarries in Wales many million hundredweights of waste slate have accumulated; it is used as a raw material for brick-making. The slate in question is nothing but highly compressed clay, in which condition it has lost the property of taking up water, and hence is no longer plastic. It can thus only be worked into bricks by dry or semi-dry presses, and the bricks must be burnt until they sinter, in order that they may acquire solidity. The waste is now treated by machines specially constructed for the purpose. It produces bricks which are unsurpassed in denseness, strength, and hardness, whilst they are about 33 per cent cheaper to make than ordinary bricks. They will also bear a very high temperature. Their crushing weight is given at 1135 kilos per sq. cm. (16,500 lb. per sq. in.).

The method of making these clay bricks is as follows: The clay waste is first pulverized; the powder then falls through a perforated iron plate into a pit, from which it is raised by elevators to a higher floor, where it is mixed in a cylindrical mixer with a small quantity of water. The slightly moist material then goes to the hopper of a brick press—a dry or semi-dry press—in the moulds of which it is compressed by high pressure into bricks. The latter are taken direct from the press to the kiln and burnt.

A use has been found for the slate dust produced in the cutting and polishing machines. This is put through very fine sieves and either alone or in conjunction with French chalk is made into a stiff paste with a solution of sodium

silicate. When the paste is of the proper consistency it is placed in a cylinder and by means of a piston is forced through round holes in the end of the cylinder, thus forming long circular rods, which are cut up, laid in grooves in boards, dried, and then gently burnt in a kiln, thus forming excellent slate pencils.

Alumina and Soda from Bauxite Residues.—J. H. Ramsay and F. R. Lowe in their patent (Eng. Pat. No. 9705 of 1915) declare their invention to be as follows: It is known that the residue from bauxite, after extraction of the greater part of the aluminium oxide, still contains up to 25 per cent of alumina. Analysis shows that this residue contains the following: Loss on ignition 6-7 per cent, silica 5-6, sodium oxide 4-8, alumina 17-22, ferric oxide 48-57, titanium dioxide 6-8, lime 1-1½; the soda and part of the alumina, and silica being in the form of a double silicate. This compound can easily be decomposed, and the invention consists in the method of decomposing this sodium aluminium silicate. For this purpose carbon dioxide gas, wet or dry, sulphurous acid, or hydrochloric acid, either as a gas or in solution, or any other acid such as sulphuric acid may be employed, the aluminium oxide then being in a form easily soluble in sulphurous or acetic acid.

CHAPTER LVIII.

BROKEN PORCELAIN AND EARTHENWARE.

IN the porcelain works and also in the manufacture of fire-clay goods there is always produced a proportion of spoilt and broken ware which is ground up and mixed with fresh clay for the production of fresh ware. The introduction of this burnt material is found extremely beneficial, as it reduces the shrinkage of the material during drying and thus produces better casts which are less liable to crack during drying and burning.

Broken Porcelain and Pottery with White or Coloured Glaze.—In the journal of this industry it is proposed to use these fragments for mosaic pavements for entrance halls, foot-paths, etc. The method is particularly suitable for roofing felt. The fragments are sorted according to colour, coarsely ground and then sieved through sieves of more or less coarse mesh. The mosaic pattern, drawn or stencilled on strong paper, is now covered or pasted over with the fragments according to size, the flat side downwards; the paper is surrounded by a rim and fluid asphalt poured on to a depth of two inches. After cooling, the paper is washed off, when the plate is finished. Large surfaces of pavements are made from separate plates, the joints being filled with melted asphalt. For this purpose pure asphaltum is not required; it is mixed with coarse sand, powdered asphalt stone, clinker, etc., and with a little lime.

The Waste from the Manufacture of Fine Earthenware.
—This is a case of utilizing the used gypsum moulds.¹ It is

¹ "Zeits. f. Thonwaaren-Industrie."

recommended to employ these moulds for fertilizing purposes, which has been found practicable. The author of the communication says: "The main water trenches are made somewhat wider and deeper than usual and piled up with a layer of old gypsum moulds, in which the water finds sufficient space to penetrate. As soon as the moulds are dissolved, which is the case in a relatively short time, the layer is renewed. With this method of fertilizing, the grass stands straighter and higher and shows more bluish-green colour, the clover between grows rapidly, the moss in wood-meadows visibly disappears, and the crop is larger than in meadows not watered with gypsum solution."

Recovery of the Waste Gold in Porcelain or Glass-works.

—All broken or spoiled porcelain or glass articles which have been gilded are carefully kept. The fragments are broken into small pieces and placed in a shallow vessel of suitable size. Sufficient *aqua regia*, made from 4 parts of hydrochloric acid and 2 parts of nitric acid, is poured on to cover the fragments completely. The vessel is covered with a similar one inverted, and the edges smeared with clay to prevent the vapours escaping. After two or three hours the upper vessel is removed to see if the gold has dissolved, but if this should not be the case, the upper vessel is again replaced and gentle heat applied by standing them in a pan of hot water. The acid is poured off, the waste washed once or twice with a little water, and the whole of the liquids mixed. Paint pots, dishes, etc., containing gold are burnt to remove the oil and treated in the same manner as the waste. Cloths containing gold are burnt and the ash treated for the recovery of the metal as described on p. 285.

Treating Graphite Crucible Shards.—In the patent granted to the Maschinenbau-Austalt, Kalk (Ger. Pat. 289,288), claim is made for a method of recovering graphite from used or broken graphite crucibles, in which the shards are crushed to the fineness of the particles of free graphite present, and the material is passed through a magnetic separator, which

extracts the magnetic slag. The remainder, which still contains dense, solid particles of slag, is treated by levigation, yielding pure foliaceous graphite. The graphite retained by the magnetic slag is recovered by fine grinding and levigation.

CHAPTER LIX.

UTILIZATION OF WASTE GLASS.

OLD glass bottles and old glass are collected by dealers and sent to the glass-works where they are broken up, and under the name of "cullet" always added to a charge of fresh materials in making glass.

WASTE PRODUCED IN GRINDING MIRRORS.

Utilization of the Polishing Sand.—In grinding glass, especially in making mirror-glass, a very fine polishing sand is used, which, after it left the apparatus, was formerly useless. The pasty consistency, and absence of plastic nature, were great obstacles to further treatment. Le Motte, a Paris engineer, has obtained a patent for the use of this waste in making a very hard building-stone. The mud from the grinding-tables, consisting of fine glass dust, quartz flour, and finely divided cast iron, is first run into settling tanks, from which the supernatant water can be removed as required. The deposit is then dried in centrifugals, mixed with fine clay powder or glass flour in a mixing and kneading-machine, pressed into moulds, and burnt at a high temperature to a very hard mass. A pressure of 300 kilos per sq. cm. (4220 lb. per sq. in.) is required, since the bricks are very porous. These bricks are not attacked by most mineral acids; they also exhibit a very considerable resistance to chloride of lime and sodium sulphate. The weight is not more than that of ordinary porous bricks. By mixing other ingredients with the sand, enamelled bricks may also be made, suitable for the decorative treatment of façades.

Another account states: The used grinding sand, containing more or less clay, which is produced in considerable

quantities in grinding mirrors, is to a great extent in such a fine state of division that it has become plastic and can be moulded whilst wet. The fine particles of glass, which have been ground off, make the mixture still easier to mould; the sand may thus not only be moulded into various shapes, but the objects produced can be burnt. The quantity of the fusible sodium silicate in the used sand is so considerable that it is sufficient, with proper burning, to cement together the grains of quartz, and thus impart to the moulded object a certain degree of strength.

The moulding, pressing, drying, and burning are done in the ordinary manner, hard bricks, hollow or solid, plain or ornamental tiles, building-stones and architectural ornaments being readily obtained. The product, which is very light—the specific gravity is about three-fifths of that of ordinary stone—exhibits no small resistance to mechanical and chemical actions.

Utilization of Broken Glass.—Posturing, Gatchy, and Geille of Paris, have proposed to use broken glass in the manufacture of pilasters.¹ A quantity of broken glass of different colours, previously broken up to a determined size, is mixed together, brought into moulds lined with a resistant material, such as silica or talc, and heated. A coherent mass is obtained, which can be dressed and cut into blocks of irregular colour. These blocks can be used as artificial marble; they are generally rough on one side, and occasionally incompletely fused, thus giving surfaces which can readily be built up with the aid of a little mortar. Handsome decorative effects may be produced whilst the blocks are still plastic. When a mould is used which can be taken apart, the pieces of glass can be so divided off that very effective coloured glass windows are obtained during the heating, in which windows the necessity of the usual lead work is avoided.

¹ "Thonindustrie-Zeitung," 1891; "Neueste Erfindungen und Erfahrungen," 1891.

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