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200

which it is sold as waterproof cloth. The vulcanisation is carried out in a water-bath at $2\frac{1}{4}$ to $2\frac{1}{2}$ atmospheres pressure, care being taken to keep the temperature constant.

After vulcanisation the sheet is unwrapped and washed.

For thread-cutting the automatic cutting-machine shown in fig. 90 is employed, with drums 450 mm. in diameter and 700 mm. long, on which the sheet, lightly coated with shellac, is rolled. On an average six such machines are required to cut 120 kilos. of thread per day, and three men are required to attend them. The cutting is followed by boiling-out (to remove free sulphur), drying, sorting, and tying into bundles, special care being taken with the boiling-out process. The drying-room should be kept well ventilated and dark,

CHAPTER V.

MANUFACTURE OF EBONITE.

HANCOCK is generally looked upon as the originator of the manufacture of ebonite. He patented his process for the vulcanisation of rubber by means of sulphur towards the beginning of the year 1843 without prejudice to the fact that Goodyear had already obtained the substance "hard-rubber"; Goodyear, however, had not gone so far as to prepare useful articles from it on a manufacturing scale.

For a long time, however, nothing more was heard of the process, since the various experiments made did not turn out favourably enough when they came to be put into practice. It was in 1851 that Goodyear, realising the importance of ebonite, took up his experiments again and succeeded in preparing a substance which was very suitable for articles in which, in addition to elasticity, the qualities of durability, ease of working, and chemical stability are essential. Goodyear's ebonite of that date consisted of a mixture of Para, magnesia, whiting, shellac, lead or zinc salts, and sulphur, these ingredients being intimately mixed together and run out into strips which were vulcanised at a fairly high temperature. The product obtained was dark in colour and hard, similar to jet or horn, and lent itself to being worked quite well. Gradually Goodyear omitted from his composition all the fillers except sulphur, his mixing now consisting of rubber and sulphur only; at the same time he raised the temperature of vulcanisation to about 165° C., and so arrived at a perfect ebonite. The problem still remained of finding a material with which to cover the plastic hard-rubber composition before vulcanisation, and with the discovery by L. Otto P. Meyer in 1854 that tinfoil was eminently suitable for this purpose, ebonite manufacture took its place amongst the industries in which manufacture in bulk can be successfully carried. out, and, advancing steadily, soon won for itself a large market.

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For these reasons Charles Goodyear and L. Otto P. Meyer must be regarded as the real founders of the hard-rubber industry.

Hard rubber, also called ebonite or vulcanite, is highly vulcanised rubber containing a large proportion of sulphur. The best qualities consist merely of rubber and sulphur. In the lower qualities, however, ebonite waste, ground to dust, is also used, together with mineral and other compounds and rubber substitutes, which are enumerated below.

Ebonite, unless otherwise coloured by the addition of pigments to the mixing, is of a rich deep black colour; it is capable of takinga high polish, and is easy to work mechanically; it is powerfully electrified by friction, and is a good insulator. It is diathermanous (transparent to heat rays) in a considerable degree, and its refractive power for radiation is high. Its refractive index is nearly as high as that of flint glass, and reaches as high a value as 1.56; its specific heat is 0.331249; its mean coefficient of expansion between 0° and 18° C. reaches 0.0000636, its coefficient of cubical expansion being greater than that of mercury at increasing temperature. The more important chemical behaviour of ebonite is in line with these well-known physical properties. It is very stable towards chemical reagents, more particularly when it contains no other ingredients than rubber and sulphur. To this indifference towards the action of acids and alkalies hard rubber owes its great importance and usefulness in chemical industry, especially in the form of pipes for conveying acids, and of vessels of different kinds. In a compact mass it is very stable towards air, light, and changes of temperature; it can be softened in hot water, and in this condition can be easily bent; on prolonged heating above 180° C. it loses its valuable properties and slowly carbonises, yielding no intermediate products in the process. It swells up slightly in carbon bisulphide and in coal-tar solvents, but does not dissolve appreciably in them; in general it is very stable towards most solvents of rubber.

The valuable property possessed by ebonite of becoming slightly soft when heated and when in that condition of taking up slight impressions, which become fixed on cooling, is made use of in the manufacture of embossed sheet, which may be very varied in form and design, and is a valuable manufacturing material for a number of trades.

The actual technical manipulation of this article will be very thoroughly dealt with in the following pages, for the manufacture of ebonite is one of the most difficult branches of the rubber industry. The raw material for use in this branch must be purified with the very greatest care, and in particular the raw rubber. The reason for this is that when the ebonite comes to be polished later on any small particles of sand or dust which may be present become evident as projections from its surface. Hence it is necessary as a prime condition for success that the shops in which ebonite goods are made up should be absolutely dust-free.

The manufacturing process consists of the following stages :--

- 1. Mixing the rubber compound.
- 2. Rolling into the form of sheet.
- 3. Making up the various articles.
- 4. Vulcanisation.

And in addition there is the working up of the finished articles (on the lathe, etc.), milling, etc., buffing and polishing or rubbing down with oil. The process of mixing is carried out in exactly the same way as in the case of soft-rubber mixings. The washed rubber used, which must be absolutely free from sand, may be either Para, Columbian, Congo-Lopori, Madagascar, Borneo, or good Niggers, etc., according to the quality. Of these sorts, that which, after Para, gives the best deep black polish, is Madagascar. The sulphur, which is the most important ingredient added to the hard-rubber mixing, should be mixed into the rubber as uniformly as possible. The points of greatest importance in connection with the sulphur itself are, first, its fineness, and secondly, its freedom from acid, which has a most unpleasant effect upon hard-rubber mixings, particularly those which do not contain magnesia usta or other neutralising agent. Flowers of sulphur nearly always contain traces of acid, and on storage will often become still more strongly acid; this conditions the presence of a certain amount of moisture which leads to the production of porous, badly-marked aud faulty goods. Freedom from grit is also a most essential quality in the sulphur to be used, particularly in the case of goods which have afterwards to be polished. In mixings of lower quality finely ground hard-rubber waste-dust-is an important ingredient, and the preparation of this material should be most carefully supervised. On account of its importance the preparation is described separately in the following section.

Preparation of Ebonite Dust.—The ebonite waste is sorted into the following classes :--

1. Waste capable of taking a polish, consisting of rubber and sulphur only.

2. Waste capable of taking a polish, containing rubber, sulphur, and hard-rubber dust.

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3. Waste not susceptible to polishing, containing mineral ingredients.

This system of classification cannot, of course, be strictly carried out; in class 1, for example, waste containing a certain amount of oil or resin may also be included without disadvantage. Class 1 waste is used in mixings for polished goods, class 2 waste for lower quality polished goods, and class 3 for "mechanical" ebonite goods which are finished without a polish. It is in the nature of things that, generally speaking, every factory works up its own waste to the best advantage, and waste bought in is consigned on sorting to a lower class, for safety's sake, albeit that owing to the employment of trade marks it is possible to appraise waste branded

with certain marks at a higher value, just as in the case of old rubber shoes.

The sorted waste, after being broken up into small pièces in the stone crusher (fig. 91), is introduced into a boiling dilute solution of caustic soda, in order to remove any dirt adhering to it. The small fragments are then washed and dried, and passed on to the "Kaiser" mill (fig. 92), which mills them into very small granules about 1 mm. across. This machine is most conveniently raised up on a

Fig. 91. which is c

pedestal, which is closed in all round and into which the milled waste passes, the "Kaiser" mill throwing out the granules at the bottom through fixed, interchangeable steel grids. The hardrubber shot óbtained in this way is now transferred first to the simple but powerful milling-machine, with rolls 500 mm. in diameter and 60 cm. long, shown in fig. 93. The rolls can be steam-heated or water-cooled. The main condition for obtaining powerful friction between the rolls consists in correctly choosing the speed ratios of the drive, otherwise the consumption of energy may reach as high a figure as 50 h.p., which would render dust manufacture a very costly business. A hopper to take the material to be milled is fixed above the rolls. The hard-rubber granules are milled until a product as fine as flour is obtained, the rolls being closed up gradually during the process. This flour is, however,

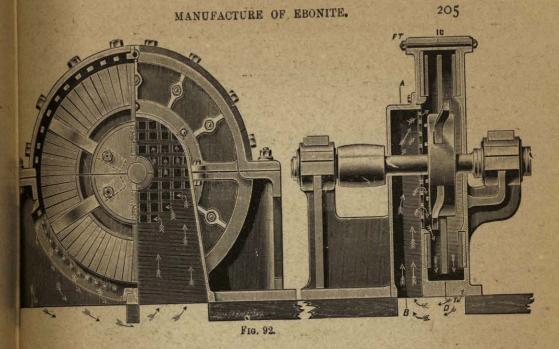


FIG. 93.

MANUFACTURE OF EBONITE.

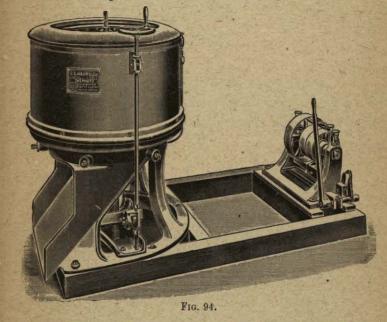
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always mixed with coarser particles from which it must be separated by means of a blast of air or by centrifugal action. For this purpose the plant employed consists of a ventilating shaft together with means for producing the air-blast, and space for separating out the coarser particles, allowing the fine dust to pass on to the filtering shaft. The hard-rubber flour to be separated is drawn by means of an exhaust-fan from the chest below the milling-rolls through a trunk, and falls into a hopper placed close up to the ventilating shaft. Two smooth wooden rollers close the mouth of the hopper, and as they revolve allow only so much of the ground ebonite to pass through as they can distribute. A special fan blows a blast of air into the fan shaft, which can be regulated by means of valves, and this passes through the valves to · the outlet, taking with it at this point the powder falling from the hopper. The fine dust is carried forward some distance before settling to the ground, while the coarser dust drops in the neighbourhood of the hopper, and is returned to the mills to be re-ground. On the other hand, the fine dust is carried forward by the air up to the filter, where it collects on the filter flannels, while the air after passing through a "Cyclone" is led into the shaft and so away. In this way two kinds of dust are obtained, one of which the finer, is used in mixings of a corresponding quality, while the other sort is used only in ordinary polished qualities. Instead of this air-separation method, the centrifugal machine can be used for separating the dust. This machine, illustrated in fig. 94, in addition to the basket, has inserted a fine wire sieve and a flannel filter. These centrifugal machines are specially made for the purpose by the firm of Haubold. The details of procedure are of a very simple nature, and need not be described. Before, however, the dust is ready to be added to the mixing it is tested on a wire sieve, and filtered through a magnetic sieve so as to remove every particle of iron from it.

1. The Ebonite Mixing.—In the case of the higher qualities the ebonite mixing consists roughly of the following ingredients:—

A. Para Sulphur Linseed oil Wax	· . 10,000 gms. · . 3,000 ,, · . 200 ,, · . 250 ,,	B. Para Madagascar Sulphur . Linseed oil		· · · · ·	2,000 gms. 3,000 ,, 2,000 ,, 200 ,,
		Wax	136		500 "

In the case of Para the amount of sulphur is not allowed to exceed the percentage given, since it has been found a suitable one to transform Para into ebonite by vulcanising for six hours in the water-bath, with steam at a temperature of 135° C., slowly rising, during the last hour of heating; to 140° C. The results of a series of experiments with different kinds of rubber, mixed with ebonite dust and sulphur, are given in the tables which follow. From these tables it will be seen that with a constant percentage of sulphur a longer time of cure did not give equally good results, but that in order to effect this the amount of sulphur had to be increased, a fact due in some measure to the resin-content of the raw rubber. The experiments were carried out with sheets 2 mm. thick, 5 cm. wide and 20 cm. long. Each sheet was tested in an apparatus which slowly bends the sheet until it breaks. The movement of the spindle is communicated to a pointer moving on a



graduated dial. The figures obtained show the amount of bending at the breaking-point.

From the second table (p. 209) can be seen what influence certain quantities of sulphur and other ingredients have on the strength and structure of ebonite compounds made from different sorts of rubber.

Linseed oil, well boiled and free from water, or "white winter" (cotton seed) oil, is added with the object of improving the polish; on the other hand, by adding a higher percentage of oil and adjusting the amount of sulphur accordingly, that is to say, increasing it, substitute is formed.

In order to produce a horny cut or fracture, and to facilitate the further working up—turning, drilling, sawing—a certain amount of white wax is added to the rubber mixing.

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To the cheaper qualities, especially for mechanical purposes, substitutes, asphaltum, pitch, and resins may be added, and in order to be able to make better use of moulds, magnesia usta.

Mixing is best done in separate stages, the sulphur and dust being first worked in, and the oil added slowly afterwards. When reclaimed rubber is used this should first be mixed with the raw rubber, and this holds good also for substitute. Care must be taken when mixing to avoid flaking, and the more finely the ingredients are worked in the cleaner will be the product. Lime should always be avoided, magnesia usta being used in preference where some such agent is necessary.

Kind of Rubber.	Sulphur, per cent.	Dust, per cent. Vulcanisation in Water-bath, °C,		Relative Breaking Strain.	Fracture.	
Para	20		¹ / ₂ hour, rising 8 hours at 135	5640	Smooth to jagged.	
73	23	The state of	1 hour ,, 140 8 hours ,, 135	5694	the Constanting	
,,	35		61/2 ,, ,, 140	6101	0 0	
• 17	30		6 ,, ,, 135	7848	Horn-like polish.	
>>*	20	10	7 ,, ,, 135	5713	Jagged.	
"	20	15	7 ,, ,, 135	5667	11	
3.9	20	25	6 ,, ,, 135	6217	Smooth.	
2.5	25 25	10	6 ,, ,, 135	6618	1)	
"	25	15	5 ,, ,, 135	6213	57	
2.9	30	25 10	5 ,, ,, 135 5 ,, ,, 14)	6022	· · ·	
**	30	10	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	7486	Horny.	
. ,,	30	25		7026 5004	Hard.	
23	30	25	4 ,, ,, 140 6 ,, ,, 140	4841	maru.	
.,	40	25	$3\frac{1}{2}$,, ,, 140	4109	Splintery, brittle.	

The second stage in the manufacture consists in running the sheet, starting with the mixed rubber, which has been quite uniformly warmed up and kneaded. The sheet is, in most instances, doubled on the doubling calenders until it has reached a thickness when it can be dealt with on the doubling rolls, and it is then laid in sheet form on racks and kept ready to be further worked up. In running this sheet special care must be taken that no bubbles of air are included between the successive layers of the sheet, and that there are no markings on the surface, due to irregular passage through the rolls; if these defects exist in the calendered sheet the result is the formation of blisters, and irregular expansion and contraction of the sheet on curing. Once the sheets have been laid out on the cloth racks great care must be taken to protect them from dust and damp.

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p		-					the second second	
		Exfent of bending at fracture.		Extent of bending at fracture.		Extent of bending at fracture.		Extent of bending at fracture.
Lagos.	50	136	50 20	126	40 10 10	120	50 10 10	130
Liberia.	. 60	116	50	105	50 10	115	60 10	110
Niggers.	55	122	40 30	118	55 10 10	119	55 10 10	116
Batanga. Niggers.	50	130 ·	50 20	122	50 10 10	120	50 10 10	120
Borneo.	50	144	40 25	136	40 10 10	140	50 10	141
Madagascar.	40	150	35 25	142	35 10 10	142	40 10 10	144
Upper Congo.	45	150	40 20,	140	40 10 10	145	50 10 10	147
Lopori.	45	149	· 45 10	140	40 10 10	142	50 10 10	145
Columbia. Lopori.	35	152	30 20	148	30 10 10	150	35 10 10	148
Para.	30	156	30 10	.151	25 10 10	150	30 10	152
Ingredients added, per cent.	Sulphur		Sulphur . Ebonite dust .		Sulphur Ebonite dust Pumice		Sulphur	

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We have now to consider the third step in the manufacture of ebonite, namely, the making-up of the various articles, and as a matter of fact ebonite sheet is, in the case of many articles, the material with which the actual preparation of those articles begins. In the following paragraphs, therefore, the process of manufacture of such sheet is described in detail. The manufacture must be carried out in shops absolutely free from dust, shops on the upper floor being most suitable for the purpose.

In order to prepare ebonite sheet the following process, which is found to give good results in every way, is employed. The sheet in question is not rolled up from separate layers to the required thickness on a heated bench, but is doubled on the doubling calenders direct from sheet $\frac{1}{2}$ mm. thick, a compact sheet free from blisters

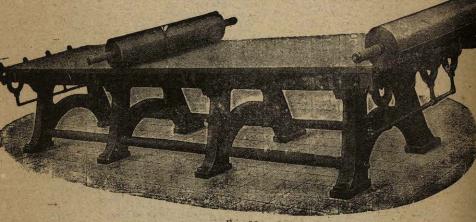


Fig. 95.

being thus produced. The sheet is then taken for further manipulation to the hot-bench, the ordinary form of which, shown in fig. 95, has long been in use. This hot-bench consists of a castiron plate, planed perfectly smooth and provided with interior channels for the purpose of heating it uniformly by means of steam. The chief use of the hot-plate is to warm up the rubber sheet so as to cause it to shrink, and prevent its shrinking during vulcanisation, and so to produce a uniform sheet. A second purpose served by the plate is, however, that of a bench on which the sheet is coated with tinfoil. This is done by means of a heavy iron roller worked by two men, the roller making the sheet uniform in thickness and homogeneous in texture, while at the same time forcing the air out from between the tinfoil and the rubber. By this means the tinfoil is hermetically sealed on to the rubber at the edges, and thus the polished surface of the foil is communicated

to the sheet of ebonite, and the surface of the sheet is kept from contact with water during the cure. Another advantage attending the use of tinfoil is that the polish obtained on the vulcanised sheet is very uniform and far superior in quality to any that could be obtained by polishing processes subsequent to vulcanisation. Well-trained hands are, however, necessary in order to successfully carry through this method of manufacture; the heavy rollers used are likely, in particular, to contribute a great deal towards mishaps and defective manufacture; their weight is sufficient, if they are moved unevenly or in a jerky fashion, or crookedly across the sheet, to produce a very uneven surface marked by wave-like depressions and elevations, and by pittings or concavities due to the pressure of imprisoned air. If the tinfoil is not put on evenly it will crease and form blisters, these giving rise in their turn to spots on the surface of the sheet, where the polish will vary in quality or degree. In order to surmount these difficulties, and at the same time to economise labour, a hot-plate has been constructed in which the roller is moved mechanically (system of Haubold and Heil). The manufacture in this case proceeds as follows :- The tinfoil in the form of a sheet twice the length of the rubber sheet to be covered, and folded in two, is lightly, evenly, and thinly coated with absolutely anhydrous linseed or solar oil on the side which is to come in contact with the sheet of rubber. The half-sheet as far as the fold is now laid on the hot-plate, and slowly covered with the sheet of rubber of the requisite thickness, by rolling the latter on to it; the sheet is then allowed to remain a few minutes for shrinking. The other half of the sheet of foil, beyond the fold, which is to cover the upper surface of the rubber sheet, is now laid smoothly over the roller in such a way that as the roller moves forward the tinfoil moves with it and is slowly laid on the sheet of rubber and firmly rolled down by the roller. The whole of this manipulation is carried out by the machine shown in fig. 96. The roller; about 300 mm. in diameter, is, as indicated in the diagram, moved forward and back again automatically, and is then automatically cut out. The two side-edges, which have to be closed up air-tight by the tinfoil, are pressed together by a small auxiliary roller, which can be adjusted to any width and thickness of sheet.

In this way a sheet absolutely uniform in surface and thickness can be prepared; it is safest to cure such sheets in the water-bath. The thickness of the sheet which can be made in this way varies from $\frac{3}{10}$ mm. to 15 mm. Thicker sheet should receive a preliminary vulcanisation under the press, as referred to below. In water-