

care must be taken to have the rubber mixing worked up and warmed uniformly, so that it may lie evenly round the roll, and not in too soft or sticky a condition, so that the friction roll can remove it without difficulty. Sticking to the middle roll must in all cases be avoided; it indicates that the particular mixing is not suitable for calendering. With few exceptions the fault lies in having the middle roll too hot. One of the chief aims should always be to keep feeding in fresh quantities of rubber regularly, and not too much should be fed in at a time. It is also essential to success to have the cloth rolled up evenly and tightly on the wooden roller before passing it through the calenders, so that no creases are formed as the cloth is unrolled, and to see that the fabric does not run crooked, which would lead to its getting torn. In rolling up the cloth, as also in dealing with the ordinary running-cloths, it is best to make use of a machine which should always be provided with a calendering plant. This machine has a large heating drum over which the cloth or fabric is carried in order to dry it thoroughly, moisture being capable of great mischief under these circumstances. Behind the drum is a mechanical brush enclosed in a box, by means of which the fabric is freed from loose fibres and dust. Into this the fabric passes as it comes from the heating drum, emerging on the other side, and after passing over the stretcher is tightly wound on the interchangeable rollers. In this way one is always sure of getting clean, dry fabrics.

Having now shown how the mixed rubber is worked up into the form of sheet, we propose to deal in the two following chapters with the important subjects of Vulcanisation and Mixings, and shall then proceed to consider in detail the various stages in the manufacture of a number of different articles.

CHAPTER II.

THE VULCANISATION OF RUBBER.

THE discovery of the process of vulcanisation by Charles Goodyear, an American, in 1839, was not, as one often reads, an accidental occurrence, but came about as the result of investigations which had been carried on by him for years. Goodyear, like many other men of an inventive turn of mind, kept on dabbling with rubber in spite of his numerous failures, and studied the effect of mixing all sorts of substances with it. Through this he was, undoubtedly of set purpose, led to his discovery, and as a result of the experience he had gained in the course of his investigations he recognised, on observing the effect of heat upon a mixture of rubber and sulphur, that the heating was essential to the process. It is a remarkable thing how this hard-pressed man, overwhelmed with debts, succeeded in working out his invention. That he did work it out is clearly demonstrated by the fact that in the description first published by him of his method for the "metallisation" of rubber he gave sufficient instructions for the technical preparation of perfect rubber goods, and that these instructions have even up to the present time lost no essential part of their technical importance; in every instance they are still in the main far superior to any of the processes devised by Goodyear's imitators. Thomas Hancock can only be regarded, in relation to the vulcanisation of soft rubber, as having confirmed Goodyear's results, though Hancock was actually ahead of Goodyear in his application for a patent for his alternative method. Without doubt he must be looked upon merely as the inventor of another way of carrying out Goodyear's invention (in a strictly chemical sense), but, on the other hand, he has undoubted rights to priority in the discovery of ebonite.

The discovery made by Alexander Parkes of Birmingham, in 1846, that soft rubber could be vulcanised by means of a solution of chloride of sulphur in carbon bisulphide, is also, from the chemical

point of view, an original invention. This method of "cold" vulcanisation is still as important as ever, whilst the numerous other processes which were invented during the life of Goodyear's patents have almost entirely lost what importance they ever possessed. Only Hancock's method, which consists in dipping the articles to be vulcanised in a bath of molten sulphur, is still deserving of mention. The other processes are in many instances merely modifications of Goodyear's or Hancock's, so disguised that it might be difficult at first to recognise the circumventing of Goodyear's patent. A favourite method selected for this purpose was that in which vulcanisation is apparently effected by the action of metallic sulphides, but in which it is really the free sulphur present in such sulphides that is the vulcanising agent.

The preparation of soft rubber, according to Charles Goodyear's process, consists in the mechanical admixture with the rubber of from 3 to 15 per cent. of sulphur, the mixture being subsequently heated—in practice under pressure—at a temperature of from 125° to 150° C. The time of "heating," "curing," or "vulcanising" must be varied according to the percentage of sulphur used, the nature of the rubber, the amount and the nature of the other ingredients, the way in which the heat is applied, the form of the article, and, last but not least, according to the technical effect which it is desired to produce. The preparation of ebonite necessitates, on the one hand, the addition of a much higher percentage of sulphur, and, on the other hand, a longer time of curing and higher temperatures. Although all this can be put so simply in a few words on paper, it is just as difficult in practice to find the most suitable conditions in any given case. As a matter of fact, in all factories this particular part of the business is still carried out by empirical methods, resulting from long experience, which are carefully preserved as valuable works-secrets. It is only quite recently that a little attention has been given, side by side with this rule-of-thumb, to theoretical considerations, and that this part of the manufacture has been attacked with scientific assistance. This can, however, scarcely result in a noteworthy revolution in the methods of manufacture. We have certainly gained the knowledge that rubber of any origin combines chemically with sulphur on vulcanisation; that the process is one of simple addition without substitution; that the percentage of sulphur entering into chemical combination with the rubber increases (a) with the time of vulcanisation; (b) when certain bases, such as litharge, lime, and magnesia are added to the mixing; (c) when a good (metallic) conductor of

heat is substituted for a poor one for press plates and moulds; (d) when the articles cured are of thin instead of thick rubber, etc., etc. We further know that, contrary to the statement of Clouth,¹ Para rubber vulcanises more rapidly and at lower temperatures than African sorts.

In countries where the decimal system of weights and measures is in use, it is customary to express the amount of sulphur to be added for vulcanisation in percentages on the amount of rubber; e.g., for a soft-rubber mixing with African rubber, 10 to 15 per cent. of the weight of the rubber, or for a hard-rubber mixing 30 to 50 per cent. of its weight may be specified. In order to arrive at comparable figures for the degree of vulcanisation of a rubber, C. O. Weber's proposal has been adopted, according to which the sulphur chemically combined with the rubber hydrocarbon is calculated as a percentage upon the pure rubber substance present. Suppose, for example, that analysis shows pure rubber 50 per cent., combined sulphur 1.5 per cent. Then the so-called "coefficient of vulcanisation" is $\frac{1.5 \times 100}{50} = 3$ (per cent. of the pure rubber substance).

This vulcanisation coefficient has proved of considerable value in judging samples of vulcanised rubber by analysis, and in controlling the process of vulcanisation.

The properties of rubber undergo an essential alteration on vulcanisation. The extent of the alteration varies, for the most part, directly as the coefficient of vulcanisation. On vulcanisation rubber loses its adhesiveness. As the coefficient of vulcanisation increases, so does the hardness of the rubber, up to the extent of becoming brittle; its resistance to the action of chemicals and solvents increases, its power of absorbing water diminishes, its property of becoming distended by the action of organic solvents becomes less marked. By selecting suitable conditions of vulcanisation, products possessing any degree of elasticity for any given useful purpose can be obtained. Vulcanised rubber is not nearly so sensitive to changes of temperature as is the unvulcanised substance. The colour of vulcanised rubber gradually deepens as the coefficient of vulcanisation increases until the deep black of hard rubber (ebonite) is arrived at. In goods vulcanised under pressure, vulcanisation results in a marked contraction, or decrease in volume, the extent of this increasing with the coefficient of vulcanisation.

Rubber acquires on vulcanisation a different smell from that which it possesses in the raw state; and this is, in many cases

¹ *Gummi, Guttapercha, und Balata*, 1899, p. 123.

sufficiently characteristic to permit of conclusions being drawn as to the kind of raw rubber used. In the case of rubbers which have a bad smell in the raw state, the smell often becomes intensified on vulcanisation; as, for example, in the case of "Lumps" or "Guayule."

Soft rubber has the reputation of being perfectly waterproof. It is not very well known that soft rubber undergoes a considerable change when subjected to the prolonged action of hot water; it absorbs an appreciable amount of water, becoming much lighter in colour, and suffering a marked diminution in tensile strength. At the same time its power of adhering to fabrics is greatly modified. The thinner the coating of rubber, the more pronounced is the effect of water. This property of soft rubber is utilised, to a limited extent, in the working up of old rubber.

Vulcanisation by Goodyear's method by means of sulphur can only occur at temperatures above that at which the mixture of rubber and sulphur melts. Statements in a contrary sense,¹ to the effect that a thin sheet of unvulcanised rubber containing sulphur can be vulcanised up to a certain point merely by the action of light, have proved, on re-examining the facts, to be incorrect; in no case have such sheets been found to contain a trace of chemically combined sulphur, and they therefore remain completely soluble in benzole. The error has probably arisen from the fact that the sheets in question had to be rendered plastic in the operation of mixing-in the sulphur, but gradually regained, after being kept for a long time, the original physical properties exhibited by the dry unvulcanised rubber before mastication. If pieces of "young" Para rubber about 1 mm. thick be removed from a ball, and allowed to dry gradually, the slices attain in the course of time the appearance and almost the physical properties of vulcanised rubber, and when superficially examined might be judged to be vulcanised. In the case of the unvulcanised sheet containing sulphur the illusion is naturally still more likely to take place, because the addition of sulphur partially destroys the adhesiveness of the rubber. A rubber can only be considered vulcanised if it contain chemically combined sulphur, or sulphur and chlorine. Up to the present no method of reversing the vulcanisation process is known which does not result in the breaking down of the rubber molecule. This point will be more thoroughly dealt with when the subject of "Reclaiming" is considered.

Vulcanisation by means of sulphur generally results in the combination with the rubber of only a portion of the sulphur

¹ Cf. Fr. Clouth, *Gummi, Guttapercha, und Balata*, 1899, p. 131.

added, the other portion being merely held in a kind of solution in the rubber, which is in a more or less viscous state at the vulcanising temperature, and crystallising out again on cooling. The changes which occur during the process have been microscopically examined by Pierre Breuil, who has published a number of instructive photo-micrographs of them.¹ The uncombined ("free") sulphur gives rise to the phenomenon of "blooming" or "sulphuring-up," which imparts to the goods on which it occurs a greyish appearance due to a coating of finely-divided sulphur, and which may or may not be desirable from the purchaser's point of view. Sulphuring-up can generally be prevented by using a mixing of a suitable composition. Sometimes the goods are first of all allowed to sulphur-up, the sulphur being afterwards removed by gently heating with solutions of caustic alkalis, or by other means.

As already mentioned more than once, a mixture of plastic rubber and sulphur becomes more or less viscous at the temperature of melting sulphur. This property must be taken into account in the manufacturing processes, where it is necessary to adopt some means of preventing the articles, which have been made to a given shape, from losing that shape when subjected to the vulcanising temperature; this is of especial importance in the case of so-called "open" cured goods. Generally speaking, there is not much risk of the goods actually melting down as a whole, since on the one hand the softening only advances very slowly through the mass of rubber, rubber being a bad conductor of heat, and, on the other hand, the process of vulcanisation tends more and more as it goes on to check anything of the kind; the fear is rather that when the rubber gets soft at the high temperature, the goods will tend to fall out of shape by their own weight if they are not carefully supported in some way. In some kinds of tubing which is cured in the open, this effect of the heat of vulcanisation may be recognised by the fact that the tube has lost its circular cross-section, and become more or less elliptical. This difficulty may be got over by using rubbers which cure quickly, or by the addition, where possible, of appreciable quantities of basic substances which facilitate vulcanisation, such as litharge or magnesia usta, or by increasing the proportion of sulphur in the mixing.

Nothing is yet known with absolute certainty as to how such basic substances as those just mentioned act in facilitating vulcanisation, and fantastic ideas on this subject, as well as on the similar action of metallic sulphides, are therefore in existence

¹ *Le Caoutchouc et la Guttapercha*, ii. 158 and 197.

amongst rubber specialists. We shall not occupy any space in discussing these ideas.

The vulcanisation of thin-walled rubber goods and of lightly proofed fabrics is best carried out by Alexander Parkes' process, in which chloride of sulphur is employed as the vulcanising agent, either in solution or in the form of vapour. In many instances Parkes' cold vulcanisation process is competitive with Hancock's process, in which vulcanisation is carried out in a molten sulphur bath. The practical working of these two processes will be dealt with later on.

It is a very remarkable fact that the processes of vulcanisation which have just been referred to are still carried out in exactly the same way as invented by Goodyear, Hancock, and Parkes respectively. Even with reference to certain details, as, for example, those relating to the use of magnesia usta in hard rubber (*Goodyear*) or to the solvent which it is best to use for chloride of sulphur (*Parkes*), manufacturers have, after making several departures from it, again reverted in almost every instance to the original practice of the inventor. Still it is true that considerable improvements have been made in the course of time in the methods adopted for preserving the form of goods during vulcanisation, and in the methods of applying heat to them.

The Vulcanising Shop.—Having in the last section dealt fully with the nature of vulcanisation, we shall in the present section consider the details of the arrangement of a modern vulcanising shop.

The vulcanising plant forms one of the most important items in rubber-goods manufacture, and it is essential that the shop in which the process is to be carried out should be provided, in every particular, with the most modern and most convenient arrangements that have been devised in the course of the fifty years, roughly speaking, that have elapsed since the rubber industry was founded. As already stated in the introduction (Room D, fig. 1), it is advisable to place the vulcanising plant immediately at the back of the boiler-house, so that the steam-pipes need not be unduly long, an arrangement which tends to minimise condensation in the pipes. Similarly, the shop should be close to the moulding shop, so that the heavier moulds can be moved about with as little difficulty as possible. These two points form, so to speak, the basis of the plan. The building is provided with a span roof so that as much air and light as possible can get in, and so that there are no pillars in the shop to be in the way. It is advisable to have a ridge-turret the

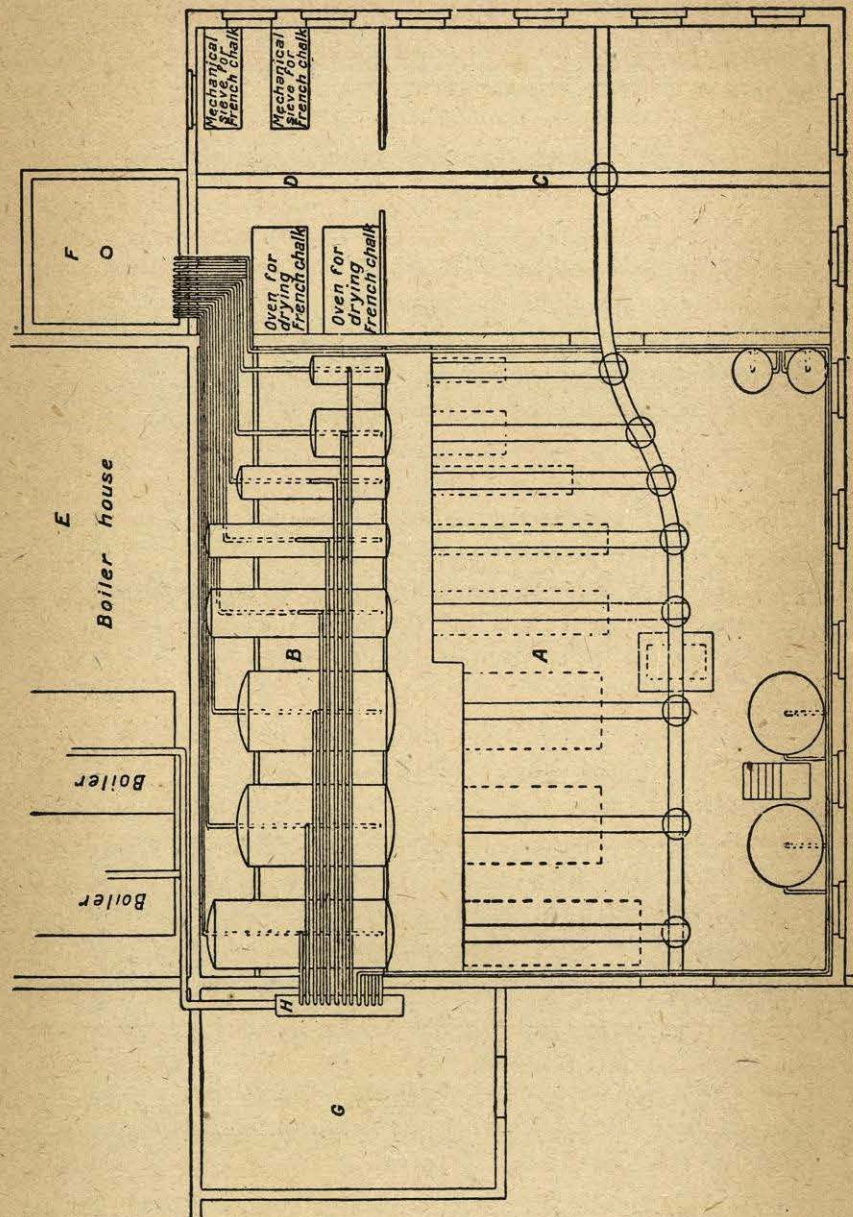
whole length of the shop, provided on both sides with glass jalousies which open very easily, in order to ensure efficient ventilation. A fan driven by an electro-motor is employed to get rid of the steam which escapes on opening the heaters. A plant arranged for a large, well-organised works, and to be put down on the lines of the accompanying plan, would be as follows:—

A mechanically driven traveller for raising and transporting the loads which are to be stacked upon the various heater trolleys runs the whole length and breadth of the vulcanising shop (A, fig. 30). In the adjoining room B are the heaters, ranged along the long side of the shop, with the fronts of the heater doors visible. The heaters themselves are therefore in a separate compartment B in room A; B contains only the heaters, each of which is well insulated. This compartment has a non-conducting top to still further protect the heaters from cooling. We also see here against the wall the heater, about one metre in diameter, which serves to receive the outlet pipes on their way to the condensing tank F.

At a point just before the outlet pipes enter the tank non-return valves are introduced. When steam is blown off from a heater the steam enters the tank, which is filled and kept fed with cold water, where it is condensed, the slight amount of steam produced being able to escape from the condensing tower, which is carried up to a height of about 10 metres, while the condensed steam runs back into the tank. All outlet pipes should be carried into the water to a distance of about two metres. The outlet valves are situated beneath the ends of the heaters in room A. By arranging and building in the heaters in this way all possibility of excessive radiation of heat from the heaters into room A is removed.

In the same room, in front of every heater, are rails on which the vulcanising trolleys run, these being sunk into the ground to a slight depth so that the top of the trolley is level with the main transport rail, which runs the whole length of the vulcanising shop and connects it with the other shops in the factory; this arrangement is such that the loaded trolleys can be run straight from the main rail, over the turntables, on to the heater trolleys, thus doing away with the heavy work of unloading and repacking in chalk. There are four upright heaters in the shop, also of course well-lagged. Two of these are provided with steps leading up to an iron platform surrounding the heater breast-high. Under the main rail track is a tank, used for cooling down the moulds, the whole trolley load being lowered into and hoisted out of the tank by means of a lifting tackle. In a smaller room the goods are packed

in chalk, the air being kept carefully free from dust by artificial ventilation. In this room are also kept various kinds of iron boxes or trays to take the goods, these being put straight on to the trolleys



and not again unpacked before being cured. They are quite ready to undergo vulcanisation for the necessary length of time, when run into their respective heaters. Another room, D, is used for drying and sifting the chalk used in the vulcanising process. In this room the trolleys are emptied, after vulcanisation, of all goods

which have been cured in chalk. The chalk is then immediately dried in the oven, put through a chain-pump into the revolving sieve, and sifted; it is then ready for further use.

A glance now at the heaters themselves. These should, if possible, be constructed to stand a steam pressure of six atmospheres, and the doors should be designed with a fairly wide flange with a recess in order to give the packing a good firm hold, so that it does not require to be renewed very often. The bolts for closing up the heater door should be fairly strong and thick, so that as few bolts as possible need be used, and the operations of opening and closing the heaters be thus more rapidly carried out. The steam supply to all the heaters is centralised; the steam pipe from which all the supply pipes are taken, and on which are also the inlet valves, manometers, thermometers and water-gauges for every heater, is set up in the control-room G, quite by itself. A similar steam pipe on the other side, fitted with similar apparatus, is used for the press shop. In arranging for the supply of steam to the heaters, and the outlets for condensed water and steam, careful attention must be directed to the pipe system. Under no circumstances should too small a pipe be used, and the outlet pipe should always be larger than the supply pipe. To ensure economical consumption of steam a Bourdon steam-trap may be introduced at the outlet.

With reference to the control-room G, it may be said that it is here that the correct conduct of the vulcanisation rests in the hands of the man in charge. In order that vulcanisation may be successful, this man must perform his duties with exactitude. The steam passes from the boiler-house, through the superheater, where it is dried, to the steam pipe H in the control-room. A steam trap is interposed between the main steam supply pipe and the steam pipe H. Projecting from this we see all the valves, the pipes from which lead to the heaters corresponding to the numbers on the valves. Manometer and thermometer tubes are brought into this room from the heaters, the scales being placed directly above the corresponding valves. In addition, there is an arrangement for introducing a mercury manometer for the purpose of checking the others. Each manometer should be provided with a recording apparatus so that the vulcanisation can be regulated at any moment, and proper control be maintained over the "rise" as well as the steady pressure. The heater having been closed, and the outlet valve adjusted, the man in room A, who should have nothing else to do than attend to the heaters, signals by means of an electric bell