

and amongst others the "Kamerun-Kautschuk Compagnie A.-G." has been registered in Berlin with a capital of three million marks.

In Asia rubber is obtained from a number of different trees, the latex from which is worked up together, as in the case of the vines. For this reason it is even more difficult than with African rubbers, leaving out of consideration the finest qualities obtained from the plantations, to determine the origin of commercial sorts of Asiatic rubbers. Amongst wild Asiatic rubber-plants *Ficus elastica* holds a premier position, but *Willoughbeia firma* and *flavescens*, *Urceola esculenta*, *Leuconotis eugenifolius*, *Calotropis gigantea*, and *Cryptostegia grandiflora* also yield rubber. The solid rubber is obtained either by skimming the latex and drying the cream so removed, or by boiling the latex until the rubber separates from it; to a great extent, also, by the addition of a kind of gypsum or other substances which have a chemical action on the latex, or by simply allowing the latex to flow from the tree and dry upon the trunk or on the ground. The value of the rubber obtained varies a great deal. In some brands it is customary to distinguish between no less than four different qualities. The rubbers obtained from indigenous Asiatic plants are usually rich in resins, and, like Africans, behave sluggishly on vulcanisation.

It has already been mentioned that *Hevea* is being successfully cultivated and employed as a rubber producer in Ceylon and the Malay Peninsula. *Ficus elastica* has also succeeded well in the Dutch Sunda islands, and intelligent treatment of the latex has already resulted in the production of a thoroughly well-prepared rubber. This plantation rubber will also become, in the near future, a permanent feature of the market, gradually increasing in quantity, for at the beginning of the year 1906 a "Borneo-Kautschuk-Compagnie A.-G." was formed in Berlin with German capital, in order to cultivate rubber in plantations.

There is no doubt that plantation rubber has a brilliant future before it. By the skimming process, which is almost universally employed on plantations, rubbers are obtained, not only in the case of *Hevea* latices, but also from *Castilloa* and *Ficus*, which leave practically nothing to be desired, and which have the distinguishing characteristic that they contain no dirt, and as a rule no appreciable quantity of proteins and putrefactive bodies, the natural resins of the particular latex being practically the only impurities present. Their permanently pale colour is also one of the decided advantages attending their use.

Latices do not contain solid rubber as such, but a substance

which is capable of being transformed into rubber partly by mechanical and partly by chemical agencies. By extracting a latex with ether, and carefully evaporating the ether from the extract, the rubber-yielding substance is left behind as a thick oil, which is transformed into solid rubber when rubbed with a glass rod or treated with a little acid. The change which takes place during this solidification is at present regarded as a process of polymerisation.

The "rubber-substance" proper is an unsaturated hydrocarbon, or possibly, to speak more correctly, a mixture of unsaturated hydrocarbons. According to the investigations of C. Harries, caoutchouc appears to be a polymer of cyclo-dimethyloctadiene. In addition to this "rubber-substance," rubber contains varying proportions of resins, from which it may be freed without difficulty by extraction with hot acetone in a Soxhlet or similar apparatus, provided that only thin, washed and dried sheeted rubber be used for the extraction. If after this extraction with acetone the residue be further extracted with carbon bisulphide, chloroform, or some other solvent of rubber, the "rubber-substance" dissolves and goes into the extract, and there remains a residue consisting partly of organic, partly of inorganic substances. This residue frequently contains appreciable quantities of nitrogen-containing substance, which is designated, in general terms, mucilage or protein substance. If care has been taken, in coagulating the rubber, to keep it as free as possible from albuminoids—as in the instance of Ceylon Para—traces, at most, of nitrogenous matter are found in the residue, which does not, when incinerated, give off the characteristic smell of burning hair or horn. If, however, coagulation has been carried out in such a way as to retain practically the whole of the albuminoids of the latex in the rubber, the insoluble residue gives a very marked smell of burning hair or horn when incinerated. The inorganic substances mentioned as being present in the insoluble residue, or in the ash, may consist partly of such impurities as were not removed by the washing process, but are also partly derived from organic salts contained in the rubber.¹ Para rubber generally contains (chiefly) calcium salts, while African rubbers contain ferrous salts, and Ceara magnesium salts.

Generally speaking, it is desirable that a rubber should contain only a low percentage of resin, and as little albuminoid and other organic impurity as possible. A small amount of albuminoid matter, provided it is in good condition and free from bad

¹ Henriques, *Der Kautschuk und seine Quellen*. Dresden, 1899, p. 25.

smell, as, for example, in the case of Para, is, of course, quite harmless. Further, the rule may be laid down that the commercial value of a rubber as well as its physical properties—especially after vulcanisation—are roughly proportional to the percentage of rubber hydrocarbons present in it. This, as is well known, is likewise true for different kinds of guttapercha. This statement is, of course, only strictly true for cases where the rubber hydrocarbons do not differ from one another very much in their degree of polymerisation. Valuation on the results of chemical analysis does not, however, do away with the necessity of making certain physical and manufacturing tests. One is unable to decide from the results of a chemical examination whether a particular rubber will be certain to yield on vulcanisation a floating product such as will bear some weighting with pigment, or whether the ebonite prepared from a given rubber will take a good polish or not. Every branch of the rubber industry makes special demands on the rubber to be used in it, and suitable tests must be adapted to these special demands. To this circumstance must be attributed the fact that while one manufacturer swears by a particular brand of rubber, another finds it to be of quite inferior merit, simply because it is quite unsuitable for his particular purposes. In many instances when judging of the usefulness of a rubber, another factor comes in, to which just as much importance has to be attached as to the results of chemical analysis or of practical tests, the question, namely, as to whether the rubber under consideration is always to be had in sufficient quantity. Large factories produce certain goods on such a colossal scale that they cannot risk basing all their calculations upon the use of certain rubbers, if the sorts in question cannot be purchased without difficulty at any time and in sufficiently large quantity. For this reason the smaller factories stand in the advantageous position of being able to cover a considerable portion of their requirements in crude rubber by opportune purchases of small parcels. When these facts are taken into consideration, it is easy to understand why certain sorts—for example, "Massai niggers"—upon which large factories can rely are regularly purchased at prices which do not actually represent their true value, while small lots of the finest Congo sorts can be had comparatively cheap.

In addition to true rubbers, "pseudo"-rubbers are used in the rubber industry to quite a large extent. These "pseudo"-rubbers consist essentially of resins containing a small percentage of a rubber hydrocarbon, and come on to the market as "Paste" or

"Flake." Of late these pastes have been coming not only from Liberia, the Gold Coast, Gaboon, and the neighbouring countries, but also from Central America, under the name of "Mono Rubber." Besk or Pontianac, also called Gutta Jelutong or Dead Borneo, is interesting from the fact that the resins, of which it chiefly consists, behave exactly like the resins of true guttapercha and are probably closely allied to them.

The following table gives some analytical data for a number of different kinds of raw rubber. The very complete raw rubber tables of Drs. Henriques and Soskin, given in Herbst's *Gummikalender*¹ from year to year, may be referred to in this connection. These tables give not only accurate information as to the geographical origin, trade-name, export towns and botanical origin of every single commercial sort, but also include important notes as to their appearance and properties, average price, mean loss on washing, and resin-content.

| Name of Rubber. | In the Washed and Dried Rubber. | | | | |
|-----------------------|---------------------------------|-----------|-----------|------------|--------------|
| | Resins. | Oxygen. | Protein. | Inorganic. | Pure rubber. |
| | per cent. | per cent. | per cent. | per cent. | per cent. |
| Para, fine | 1.9 | 2.2 | 2.9 | 1.1 | 91.9 |
| „ entrefine | 2.0 | 2.3 | 4.1 | 1.3 | 90.3 |
| Ceara | 2.1 | 2.4 | 3.3 | 4.5 | 87.7 |
| Columbian | 6.8 | 6.8 | 3.5 | 1.0 | 81.9 |
| West Indian | 8.6 | 7.2 | 10.4 | 3.2 | 70.6 |
| Massai | 6.4 | 6.6 | 7.4 | 2.8 | 76.8 |
| Kassai | 5.6 | 5.4 | 7.9 | 2.1 | 79.0 |
| Upper Congo | 6.1 | 5.6 | 12.4 | 3.2 | 72.7 |
| Madagascar | 7.2 | 5.8 | 6.8 | 1.2 | 79.0 |
| Batanga | 12.4 | 8.9 | 12.7 | 2.7 | 63.3 |
| Thimbles | 9.1 | 7.8 | 8.4 | 3.6 | 71.1 |
| Lopori | 5.9 | 5.7 | 7.2 | 1.8 | 79.4 |
| Mozambique | 5.8 | 5.8 | 6.1 | 1.9 | 80.4 |
| Borneo, I.a | 8.0 | 5.9 | 10.8 | 2.2 | 73.1 |
| „ III.a | 15.0 | 9.0 | 14.9 | 3.8 | 57.3 |

The Physical and Chemical Properties of Rubber.—The physical and the chemical properties of rubber are of almost equal importance, so far as the rubber industry is concerned, though one particular chemical property is of outstanding interest, the property, namely, of combining with sulphur or chloride of sulphur to form vulcanised rubber.

Rubber, well-cleansed and dried, has a specific gravity of from 0.925 to 0.967 in the case of samples which have been

¹ Steinkopff & Springer, Dresden.

carefully freed from enclosed air. Rubber is a bad conductor of heat and electricity, and extensive use is made of its electrical insulating power. By friction or pressure rubber becomes electrified, this property being put to a practical use in the case of certain electrical machines in which ebonite discs are used instead of glass.

Good sorts of rubber are transparent in thin sheets, particularly when stretched. Thicker sheets have a yellowish-white to yellowish-brown colour. Rubber may be coloured by admixture with pigments. The mineral pigments are specially suitable for colouring purposes, the lakes of the aniline dyes, on a barium sulphate or alumina base, being almost completely absorbed, even when added in considerable quantity. The use of aniline lakes is possible, however, when it is a question of producing an ultramarine shade, or of colouring the surfaces of goods. The results which are obtained by the admixture of pigments with rubber may, in a sense, be compared with those obtained on mixing the same pigments with oil, when one is dealing with colours which in the dry state lack brilliancy. Further reference will be made later to the changes of colour undergone by pigments under the conditions of hot vulcanisation, a subject of great importance.

At ordinary temperatures—say about 17° C.—unvulcanised rubber has considerable elasticity and pliability. When subjected to low temperatures its elasticity is temporarily destroyed, as is also its pliability, though to a somewhat less degree. When, however, the rubber once more attains the ordinary temperature, these two properties are completely restored. If a strip of unvulcanised rubber be stretched and while in that condition be moistened with water and the latter caused to evaporate rapidly, the rubber remains in its extended condition. When gently heated, unvulcanised rubber softens, and can then to a certain extent be welded together. In a similar manner rubber may be formed into compact masses by powerful compression, especially at surfaces which have been freshly cut. This property also belongs, though in a less degree, to lightly vulcanised rubber. When unvulcanised rubber is gently warmed and kneaded (masticated) it gradually attains a more and more doughy, highly plastic condition, apparently undergoing a process of depolymerisation, in the course of which the molecules, originally very complex, become increasingly simplified. Extensive use is made of this property of plasticity, in a variety of ways, during the manufacture of rubber goods. Rubber

which has been rendered moderately plastic gradually reverts, on cooling and storage, to its former elastic condition. When unvulcanised rubber is heated slightly above the melting-point of sulphur, it becomes soft, and will then dissolve considerable quantities of sulphur, at first without showing any signs of vulcanisation. If, however, the molten sulphur be allowed to interact with the softened rubber for a sufficient length of time, or at a somewhat higher temperature, chemical combination between the sulphur and the rubber gradually takes place. This process is termed "vulcanisation," and consists in the simple "addition" of sulphur to the unsaturated rubber hydrocarbon, no substitution, with its consequent elimination of hydrogen sulphide, taking place. If hydrogen sulphide or analogous compounds be produced during vulcanisation, their formation must be attributed either to the presence of some resinous or other foreign substance, or to the correct time or temperature of vulcanisation being considerably exceeded, resulting in decomposition of the vulcanised rubber, accompanied by a breaking-down of the rubber molecule. The vulcanisation of rubber is dealt with more fully later on.

When rubber is melted it remains soft and sticky on cooling; when ignited, it burns with a smoky flame. In the dry distillation of rubber a number of hydrocarbons are formed, and upon the nature of some of these erroneous conclusions were formerly based as to the chemical constitution of the rubber molecule, which was regarded as a polymer of "isoprene."¹ Professor Tilden has, moreover, stated that he obtained synthetic rubber from isoprene by polymerisation, but attempts which have since been made to repeat his experiments have not resulted in the production of rubber. As already mentioned, rubber may be regarded with a fair degree of certainty—according to Harries' investigations—as a polymeride of cyclo-dimethyloctadiene.

In certain cases rubber is vulcanised by means of chloride of sulphur, instead of molten sulphur, either in solution or in the form of vapour. This so-called "cold" vulcanisation depends upon the chemical addition of sulphur *plus* chlorine to the unsaturated rubber hydrocarbon, also without substitution. An account of this process also will be given in the chapter on vulcanisation. A number of other addition products of the rubber hydrocarbon are known; for example, those with bromine, oxides of nitrogen, and, in particular, ozone. A while ago it looked as though the nitrogen oxide-addition products would prove to be of great service in

¹ See Ditmar, *Der pyrogene Zerfall des Kautschuks*, Dresden, 1904.

rubber analysis, but the expectations formed in this direction have so far remained unfulfilled. [The methods which involve the use of the bromide would appear to be more hopeful.]

Rubber which has been vulcanised to the stage of soft rubber, and which is therefore in reality only partially vulcanised rubber, remains unsaturated to a greater or less extent, and can therefore be vulcanised still further without any difficulty, until the stage of hard rubber (ebonite) is reached. The activity of partially vulcanised rubber due to its remaining double linkages, results also in its ready oxidation by the oxygen of the air, and this is essentially the cause of the perishing of soft rubber. This oxidation is favoured by the action of sunlight and high temperatures, as well as by admixtures which increase the porosity of the rubber. Further, rapid oxidation may be brought about by the action of a solution of hydrogen peroxide in ether or acetone. Contrary to a widely-spread notion, a comparatively high percentage of resins in a rubber does not affect the durability of the goods made from it, provided that it has received correct treatment and has been carefully vulcanised; at any rate, the resin content *per se* does not facilitate oxidation. There is just as little accuracy in the oft-repeated assertion that high resin-content in a rubber brings about porosity in the goods made from it. By using the right proportion of sulphur, and selecting the temperature of vulcanisation with care, products free from pores can be made from rubbers rich in resins.

Rubber is not appreciably affected either by alkalis, or by dilute acids. Strong acids, which act as dehydrating agents, and particularly sulphuric acid, char it. Strong nitric acid stains rubber a deep yellow and dissolves it, on heating gently, with decomposition. When left in contact with water for a long time rubber absorbs notable quantities of it, becoming white in colour. In strong ammonia it swells up. Most solvents for fats, such as carbon disulphide, benzol, the various distillates from petroleum, ether, the chlorides of carbon, turpentine oils, rosin oils, etc., dissolve rubber. Solution is always preceded by a considerable swelling-up of the rubber. Only carbon disulphide, benzol, coal-tar solvent naphtha, and the petroleum benzines have, however, been used technically up to now.

According to experiments made by Henriques there is scarcely an organic liquid, especially amongst those of high boiling-point, which does not act as a solvent of rubber to some extent when heated with it for any length of time. This should always

be remembered in connection with the analysis of vulcanised or unvulcanised rubber.

The Oxidation of Crude Rubber.—Crude rubber has, relatively, little tendency to oxidation. What is usually called "oxidation" in the case of crude rubber is a process which has actually nothing to do with the oxidation of rubber, for what happens is that a portion of the rubber acquires the consistency of bird-lime without any corresponding increase in the amount of resin or in the oxygen-content, as shown by analysis. This so-called oxidation is generally most noticeable in rubbers rich in nitrogen, which still contain latex, or of which the proteins are in a state of putrefactive fermentation. The heat to which it is exposed during transport has a softening action on rubber. Rubber rapidly absorbs oxygen when exposed to its action, either in solution, or when merely distended by a solvent, or when kept stretched.

Crude Rubber Storage.—For this purpose cold, dark cellars are suitable. The parcels of crude rubber are here loosely piled up, separated by wooden partitions arranged like the shelves of an oven, so that sufficient free space is left between the separate balls and heating is thus prevented. Store-rooms which are in a warm situation, or damp rooms in which moisture and water can collect on the floor, should be absolutely avoided. The floor of the store-room should, if possible, be cemented, and be inclined towards a drain.

The Mechanical Purification of Crude Rubber.—*Washing.*—As already stated when dealing with rubber-gathering, most rubbers contain a quantity of impurities mechanically mixed with them, such as sand, wood, stones, fragments of plant tissue, salts, etc., and in addition to these, as a rule, a quantity of water which is quite small in good sorts, but in other kinds, especially the cheaper ones, is much more considerable. Hence arises the need for most careful purification of the crude material in order to free it from these foreign substances before proceeding to work it up further. The greatest care should be taken to obtain as pure a washed rubber as possible, for a badly-washed material may lead to very unpleasant consequences in the course of the later stages of manufacture. For this reason the supervision of the washing department is one of the most important duties in the factory. The purification is carried out in the following manner:—The crude rubber is first put into the vessel shown in fig. 6, and described in the section on the "washing shop," where it is softened by hot water and then rinsed. The crude material as it reaches the

manufacturer is not in a suitable condition to be put straight through the washing rolls, partly because it is too hard, and partly because the separate pieces are too large. It is, however, not advisable to soften the rubber unduly by too prolonged a heating, as this would result in loss of "nerve" in the rubber, and would cause it to become sticky. Similarly it would be a great mistake to leave the rubber, once it has been softened, to lie about and get dry, since it is then very susceptible to oxidation, especially if the latex happened to contain much protein substance when coagulated. Generally speaking,

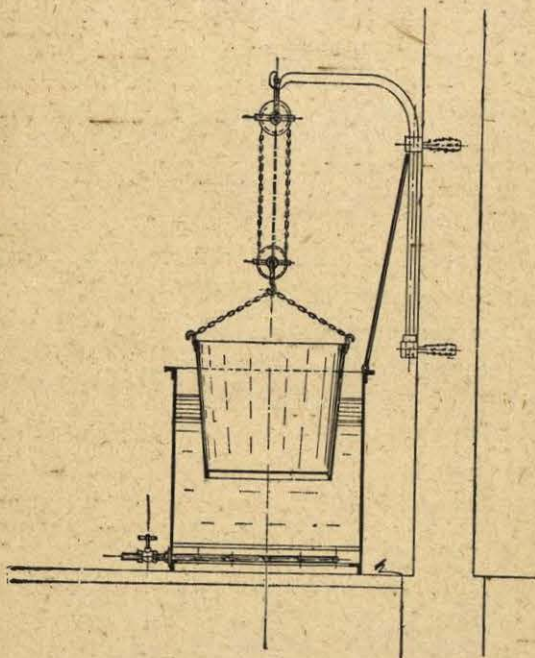


FIG. 6.

heating for from three to five hours is sufficient to soften the rubber; after this the surface is rinsed with water, to remove impurities adhering to the lumps of rubber.

If the lumps are not too large they are now at once taken to the preliminary washing rolls (crushing rolls), whereas the larger pieces are first cut up on a hand-driven cutting machine with circular knives, worked by means of crank-handles, before being put through the crushing rolls (figs. 7 and 8). The cutting machine referred to is of quite a new type, and is to be distinctly preferred to the circular saw. At this stage the actual mechanical "washing" of the raw rubber is begun. The material is brought on to the washing rolls, a detailed description of which will be given in the next section. At present it need only be said that the

crushing rolls break up the rubber into small pieces; during the process a continuous stream of water is allowed to flow between the rolls, with a two-fold object: first, to wash away a large proportion of the dirt contained in the rubber, as well as the soluble impurities; and, secondly, because the cold water prevents the rubber from becoming too hot and consequently deteriorating in quality, for in any case the cleansing process itself does not improve the "nerve" of the raw material. Still, this method

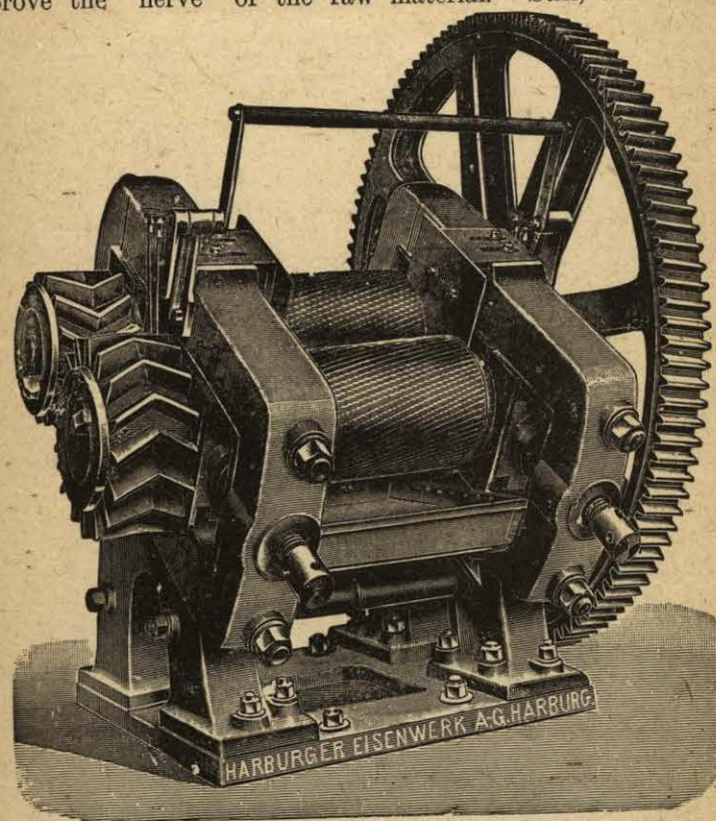


FIG. 7.

of purification is preferable to any other, and especially to the chemical method, quite apart from the enormously high working cost which would be associated with the latter, without any corresponding advantage to the quality of the rubber. When the rubber has been through the crushing rolls, the small pieces are thrown into a tank of water near at hand, and the material is then passed on to the second pair of rolls (see fig. 9), which are set up more closely than the first. Here it is broken up into still smaller fragments, water being still allowed to flow freely over the rubber the whole time. In this second stage of the