the solution of Schlippe's salt may be precipitated by means of a solution of antimonious chloride, in which case a mixture of Sb_2S_5 and Sb_2S_3 in equimolecular proportions is obtained.

Knapp's golden sulphide, so-called, or antimony cinnabar, is obtained by the action of a solution of antimonious chloride on a solution of sodium thiosulphate, and forms a deep red powder.

Ordinary golden sulphide, the product first described, is antimonic sulphide (Sb_2S_5), and imparts a yellowish-red colour to mixings in which it is employed. The mixture of sulphides next described is antimony sulpho-sulphide, and gives a vermilion red colour. The last described, antimony vermilion, is antimony oxysulphide, and the colour produced by it is a cherry-red or wine-colour.

Ordinary golden sulphide dissolves readily in cold ammonium sulphide. Knapp's golden sulphide is only partially soluble in hot ammonium sulphide, but dissolves completely in sodium sulphide solution on prolonged heating. In addition to determining the actual shade and comparing it with standard, samples of golden sulphide should be tested to see that they are absolutely neutral, and the percentage of free sulphur should also be determined, by extracting the sample, in an apparatus similar to a Soxhlet's extraction apparatus, with carbon bisulphide which has been purified by distillation over oxide of lead.[1]

Manufacture of Substitutes. — In what follows we propose to give such details of the preparation of substitutes as will enable anyone to obtain a product quite free from any objectionable features. The data to be found in technical literature on the preparation of substitutes are in part very antiquated recipes of individual chemists, and in part excerpts from patent specifications, which are certainly possessed of little value. Even respectable journals are sometimes deceived, and we find them publishing, for example, recipes according to which substitute can be prepared by treating an oil with sulphuric acid. It is not often that one is able to trace the origin of the absurdity. In the instance just cited the worthy "professional scribe" has confused *Schwefelchlorür* (chloride of sulphur) with *Schwefelsäure* (sulphuric acid), in all probability because in the particular factory from which the recipe came chloride of sulphur happened to be called for the sake of brevity *Säure* (acid), a practice common to many factories.

It would be outstepping the purpose of this book to describe every process by which a useful "substitute" can be produced. It must suffice to deal with the most important kinds of substitute as examples.

We have, in the first place, to distinguish between the two classes of substitute, (*a*) the "chlorosulphide" substitute, which is white, and (*b*) the "sulphide" substitute, which is almost black in a compact mass, but varies in colour from yellow to brown when ground up. In each class of substitute a distinction is made between "fatty" and "dry," as well as betweeen "floating" and "non-floating" qualities.

White, floating, dry substitutes are prepared from rape oil—sometimes mixed with castor oil—and chloride of sulphur in such proportions as will completely "saturate" the oil. According to Henriques, pure rape oil requires for complete "saturation" the addition of 25 per cent. of its own weight of chloride of sulphur, whilst pure castor oil requires 20 per cent.; poppyseed oil, 35 per cent.; linseed oil, 30 per cent.; cottonseed oil, 45 per cent.; and olive oil, 25 per cent. The chloride of sulphur is, however, generally diluted with benzine before adding it to the oil, or else the oil or mixture of oils is itself dissolved in benzine. By this means a spongy mass of white substitute is obtained. The preparation is carried out in capacious hemispherical earthenware pans, and the mixture is vigorously stirred, both before and after the addition of the chloride of sulphur. If, for example, 15 kilos. of castor oil and 10 kilos. of rape oil are to be used, the amount of chloride of sulphur required will be 5·5 kilos., and to this 1 kilo. of light benzine can be added with advantage. If a slightly less dry substitute be required the proportion of chloride of sulphur must be diminished. The substitute so obtained is ground up and placed on racks in a room in which it is allowed to dry off, the air in the room being rapidly renewed. Very often shallow trays containing quicklime are placed in these racks between the shelves on which the substitute lies, so that the acid vapours given off are absorbed by the lime. In other cases magnesia is dusted over the substitute with the same end in view, and also with the further object of counteracting the softening effect of large additions of white substitute to a mixing. Substitute treated in this way can, however, only be used in hot-cured goods. There are makes of substitute on the market which contain as much as 5 per cent. of magnesia, and although these are certainly specifically heavier than other sorts, the results obtained with them on vulcanisation are far superior. It is also customary in some instances to wash white substitutes, but the practice is not very frequently adopted.

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[1] *Cf.* Esch and Balla, *Chemiker Zeitung*, 1904, xxviii. No. 50.

Fatty white substitutes are prepared, as already stated, by using a lower proportion of chloride of sulphur, and sometimes by modifying the proportion of rape to castor oil at the same time. Hence there are numerous possibilities of variations in the process. One such variation may be instanced, viz. 25 kilos. of rape oil, 4·3 kilos. of chloride of sulphur, and 1 kilo. of light benzine.

It may be added that satisfactory results can also be obtained by the use of other oils, but it is impossible to go into details. Many manufacturers work out, for their own special use, a substitute which would be ill-suited for sale in the open market, but which is cheap and suits their own purposes, and can therefore be used in their own manufactures without any hesitation.

In brown substitutes, also frequently known as "black," a distinction is made between substitutes made from the raw oil and those made from blown oils. Amongst the latter the so-called "Para-factis," which contain mineral oils, vaseline or paraffin wax, are deserving of special mention.

The following recipe may be quoted as an example of the preparation of a very useful brown substitute:—100 kilos. of raw rape oil are heated at about 160° C. with 16 to 18 kilos. of sulphur in a suitable vessel provided with tipping gear. Heat may be applied either by means of a gas-ring burner or by steam; in the latter case a jacketed vessel must be used. The liquid mass is carefully stirred whilst being heated until just before the conclusion of the process, a point which is to be recognised by the liquid frothing and seething up in the vessel. The stirring is done with a paddle (generally a wooden one), and its main object is to prevent the fused sulphur from collecting on the bottom of the vessel. There is no object in using finely ground sulphur, because the sulphur first melts and sinks to the bottom of the vessel, and it therefore makes no difference whether flowers of sulphur or block sulphur is employed. Much higher proportions of sulphur than those given above may be used, but it should be borne in mind that goods manufactured from such substitutes behave differently on vulcanisation from those containing substitutes with lower proportions of sulphur. On account of the frothing which occurs, a very capacious vessel should be used. It is advisable, after the last vigorous reaction is at an end, to pour out the contents of the heating vessel into large shallow pans, where it sets to a dark mass; this when quite cool is finely ground. A substitute prepared in this manner is exceedingly elastic, and mixes well with rubber. When heated to a temperature of 145° to 155° C., and subjected to slight pressure, it again becomes viscous, and therefore distributes itself very evenly throughout the mass of rubber, in the case of goods vulcanised under high steam pressure, even if the mixing has been imperfect. By slight modifications of this process, having as their object the combination of larger proportions of sulphur with the oil, substitutes of a stiffer consistency, which are, however, at the same time harder and not so easily liquefied during vulcanisation, can be obtained; hence many processes similar to the above are in simultaneous use, in order to meet the needs of different consumers.

The brown substitutes prepared as described above are always non-floating. It is often desirable, however, to use substitutes which are specifically very light, and to meet this requirement the oils are oxidised before being submitted to a gentle sulphuration. The oils are heated for several days, a current of air being meanwhile passed through them, and they are then treated with sulphur. As a rule, however, the substitutes obtained in this way do not quite float, although some firms have succeeded in producing some fine floating substitutes solely by this method, without any addition of mineral oil or paraffin wax. The non-floating substitutes from oxidised oils are generally prepared in the rubber factory itself, whilst the really floating kinds, the so-called "Para-factis," are often referred to special substitute factories. A variety of products can be obtained, according to the duration of the oxidising process, and the amount of sulphur added. Generally speaking, it may be said that a substitute made from an oil that has been very fully oxidised, and to which a correspondingly smaller proportion of sulphur has been added, is specifically lighter, but has at the same time a considerably higher melting-point than one which has not been oxidised for so long a time. Some manufacturers, at least, prefer to use for inner tubes and similar qualities substitutes of low melting-point rather than those which melt at a higher temperature. The best plan would appear to be, therefore, to ascertain by experiment the kind of substitute most suitable for each particular purpose, and not to treat all brown substitutes alike.

It it be desired to prepare the so-called Para-factis in the factory, oxidised castor oil must be used instead of oxidised rape (according to Höhn), and to this one-third of its own weight of vaseline, or of a mixture of mineral oil and paraffin wax, must be added. The sulphuration is then carried out in the manner described.

Special kinds of substitute, to which asphaltum or ordinary pitch has been added, are used, less in rubber goods than in insulating masses for electric cables. The use of such substitutes is restricted to dark-coloured mixings.

Mention must be made of certain kinds of coloured substitutes, prepared by colouring the oil mixture before treating it with chloride of sulphur. The use of these coloured substitutes is limited to cold-cured goods, since they are destroyed by hot vulcanisation. As is well known, all chlorosulphide substitutes are converted at the higher vulcanising temperatures into dark viscous oils which, unlike those into which the brown sulphide substitutes are converted by heat, do not set again on cooling. All chlorosulphide substitutes do not decompose with equal facility. If in the manufacture of light-coloured goods it is desired to use white substitute, it is advisable to use as low a temperature as possible for vulcanisation, this being rendered possible by the use of suitable quantities of magnesia.

The colours used for colouring chlorosulphide substitutes must be stable towards acids, and non-poisonous.

Many rubber factories are obliged by local conditions to get their substitutes from special substitute factories. Such bought substitute is generally examined as follows:—White substitute is warmed with distilled water, to which is added a drop or two of a solution of phenolphthalein, rendered faintly pink by addition of a trace of alkali. If the pink colour remains—care being taken to exclude air—the substitute is practically free from acid. If the pink colour deepens, as often happens, it means that the manufacturer has added an excess of magnesia or other neutralising agent, and so has made the substitute alkaline. Nothing is to be said against this. The second test consists in comparing the carbon bisulphide extract of the substitute with that of an approved standard sample. Substitutes which are strongly alkaline should be extracted with benzol in preference to carbon bisulphide, since the latter is decomposed by alkalies, but in that case the comparison should be made with the benzol extract of the standard sample. The amount of ash or of magnesia present in a sample of substitute is also occasionally of interest to the manufacturer. Substitutes to be used for cold-cured goods must be perfectly neutral, and must therefore not contain magnesia. Substitutes which do contain magnesia are generally heavier than water, but for the same reason they are rather more stable towards heat, as may be determined by heating in a drying-oven at 150° C. In cases where the chloride of sulphur, used in the manufacture of white substitute, contained an excess of sulphur, a corresponding quantity of free sulphur is found in the benzol extract. This, however, occurs very rarely.

It scarcely ever happens that brown substitutes contain free acid, since only crude oils are used—oils, that is, which have not been refined by means of sulphuric acid—and since in the process of manufacture only neutral sulphur is employed. But individual samples of commercial products should be very carefully examined as to the percentage of constituents present which are soluble in hot acetone. This extraction is carried out in a Soxhlet or similar apparatus. The acetone extract is evaporated to dryness and the residue weighed. The residue is then extracted several times with a measured quantity of cold acetone, and the second residue dried and weighed. The difference between the weights of the first and second residues represents approximately the amount of unchanged (non-sulphurised) oil present. The second residue may consist of free sulphur and of paraffin wax, mineral oils, etc. It is treated with strong alcoholic potash until all the sulphur is dissolved, the alcohol is got rid of by evaporation, the residue thoroughly washed with hot water, and any residue of paraffin wax, etc., is weighed. It is true that only approximate numbers are obtained by this method, since it is only a rough one, but still the numbers obtained will give a sufficient indication of the nature of the substitute to an expert. A suitable quality having been selected from amongst the various commercial sorts, the application of this method of examination, combined with determinations of melting-point and specific gravity, will afford the necessary means of deciding whether a new sample of substitute is equal to that which has been in use hitherto. A brown substitute which is to be used in the manufacture of red-rubber goods should be examined as to its colour-absorbing power, and the colour of the ground product should be carefully taken into consideration. The best way of carrying out these tests is by preparing and vulcanising test-mixings.

The Treatment of Besk for use in Rubber Mixings.—The well-known unpleasant-smelling pseudo-rubber called Besk, Pontianac, dead Borneo, Gutta-Jelutong (which is now almost indispensable), always contains a great deal of sand and fragments of wood, even after it has been carefully cleaned on the washing-rolls, so much so that it is not often, or only in the lowest grade mixings, that the washed product can be used without further purification. Besk contains a small proportion of a useful rubber hydrocarbon, the isolation of which may possibly come to be regarded in the future as a paying process, but the presence of an enormous proportion of resins, together with the difficulty of removing mechanical impurities, greatly detracts from its value. There are a number of ways in which Besk can be prepared for use in rubber mixings. One of the simplest consists in dissolving the Besk in, or melting it down with, 25 to 40 per cent. of its weight of castor oil, and filtering the thick solution so obtained through sieves which can be heated. About 5 to 10 per cent. of magnesia usta is then added to the filtered mass in order to bring about good results on vulcanisation. Tar, freed from naphthalene by evaporation, is also used instead of castor-oil in other instances; in that case, however, the Besk mixture can only be used for dark goods. A more usual method of purification than that which involves the solution, melting, and filtration of the Besk, consists in forcing it through very fine sieves by means of the tube machine. Besk mixtures are generally used in order to remove the "dryness" from such mixings as contain large proportions of ingredients like barytes or whiting, and to make them easier to work up for a variety of purposes. Quite colossal quantities of Besk are also used for proofing asbestos and other fabrics in the manufacture of packings. In these cases it is merely good sticking properties that are necessary, elasticity being of quite minor importance.

Asphaltum and Pitch as Ingredients of Mixings. — Asphaltum and pitch are often added to dark mixings in order to produce "density," and to render the goods less susceptible to oxidation. These additions also facilitate the mixing of powdery ingredients, and there is less risk of the rubber getting "killed" upon the mixing-rolls. Moreover, the addition of pitch either brings about only a very slight increase in the specific gravity of the mixing, or it may even help to lower it. Natural asphaltum is not always pure enough to add directly to the mixing without further trouble. If it is very rich in mineral and, as in some instances, woody constituents, it is advisable to dissolve it in a suitable solvent, filter the solution, and then drive off the solvent again. The usual forms of extraction apparatus are most suitable for this purpose, the more modern forms being so perfect in design and construction that only a very small percentage of solvent is lost in the whole operation. Generally speaking, the use of asphaltum has fallen off very much for some considerable time, for the same effects can be produced by means of pitch, which is cheaper. In the preparation of this pitch, various kinds of tar, chiefly coal-tar, are thickened by evaporation until all traces of naphthalene are removed, and the tar is converted

into an extremely viscous, almost solid, pitch. Either hard, pure asphalt or Carnauba wax is sometimes added to the pitch in order to raise its softening point. Some makes of pitch are often met with in commerce which are thickened by the addition of resin; such pitches are not to be recommended.

The addition of pitch considerably increases the gas-tightness of rubber, and also diminishes its water-absorption; the latter property is of especial importance in cable mixings.

Fats, Oils, Paraffin and other Waxes in Rubber Mixings.—At first sight it seems absurd that, in spite of the well-known destructive action of fats and oils upon vulcanised rubber, not inconsiderable quantities of such substances should often be added to the mixings. But when it is realised that the destructive action of oils must proceed from the surface inwards in order to bring about complete destruction of the rubber mass, and that the extent of the destructive action depends very much upon the amount of oil present on the surface of the rubber, it will be seen that the oils which are added to a mixing, in quantity which is never so great as to cause the rubber mass to swell up to the extent necessary to bring about its destruction, cannot in the ordinary way cause any appreciable damage to the rubber goods in which they are used, provided they are used with discretion. Moreover, the use of oils is limited, on the whole, to those mixings which either contain a great deal of waste rubber, or a large proportion of ingredients tending to make the rubber porous. Leaving hard rubber out of account, the materials mentioned in the heading to this section are either not used at all in the finer mixings, or only in the smallest quantities.

Naturally it makes all the difference in the world whether the oils, etc., are added to the mixing before vulcanisation, or whether they act locally on the surface of the rubber mass after vulcanisation. A whole series of oils, etc., are partially sulphurised when suitably vulcanised, although it is only in the case of hard-rubber goods that the combination of oil with sulphur goes on to such an extent that one can talk about the formation of compounds similar to substitutes. Exaggerated notions as to the formation of substitute from castor oil, rape oil, etc., during vulcanisation sometimes exist amongst rubber workers; for it is very easy, by putting through an acetone extraction of such rubber mixings, to show that practically all the oil added remains, after vulcanisation, soluble in acetone; that is to say, that only a minimum quantity (or none at all) of substitute insoluble in acetone has been formed, unless, of course, very high temperatures, or ingredients which act quasi-catalytically, have been employed.

In the use of saponifiable oils in conjunction with saponifying agents such as lime, magnesia, litharge, zinc oxide, etc., the purpose which the goods are destined to serve must have a decisive importance attached to it. Such additions in notable quantity should be used in steam packings only with great caution. The use of saponifiable oils, of linseed oil in particular, in soft-rubber goods should be as far as possible avoided. Rosin oil is often deceptive in its action, a strikingly good effect being first of all produced, very soon followed, in the case of goods in the manufacture of which appreciable quantities of the oil have been used, by a ruinous hardening. Rosin oil, as is well known, is very susceptible to chemical change, and should therefore only be used in small quantities in practice. Opinions with regard to palm oil differ very widely. Whereas by some it is regarded as a very valuable addition, others consider it more dangerous than linseed oil. There is much to be said for both opinions, for very much depends upon the quantity used, and upon the many special points about the mixings in which it is employed.

The pale, heavy mineral oils, as well as vaseline and paraffin wax from petroleum, are especially largely used. These bodies are practically unaffected by the process of vulcanisation, and, provided their bromide absorption coefficient is low, they are also practically unaffected by other chemical influences, including that of the atmosphere. These statements do not apply with absolute exactitude to shale oil, or to analogous products of peat distillation. The products from these two sources corresponding to the petroleum products referred to above have generally an unpleasant smell similar to that of solar oil, which serves to indicate their presence. Some of them have an enormously high bromine absorption, which points to the presence of unsaturated hydrocarbons of the olefine series, and are therefore able to combine with sulphur when heated with it, liberating considerable quantities of sulphuretted hydrogen in the process. This reaction of the peat distillates finds application in the preparation of ichthyol products; they are of very little use for rubber goods. Ceresine, obtained from ozokerite or earth-wax, is used with advantage in rubber manufacture; unfortunately pure ceresines are rather expensive, and the wax is often adulterated. There is nothing to be said against the use of the cheaper ceresines, which are adulterated with good paraffin wax, provided they are sold as such mixtures. But besides these true "mixed" qualities of ceresine, there are many kinds on the market which are adulterated with rosin and other cheap filling and colouring matters; against these it is only necessary to utter a note of warning.

It is only in the manufacture of the various qualities of hard rubber that the use of waxes is of any very great importance, and the different kinds of wax are often used in conjunction with one another. The most frequently used are Carnauba wax and Chinese wax, although Japan wax, which belongs to another class, has recently come into fairly extensive use.

In some factories stearic acid is used instead of paraffin wax. In this connection the possibility of the goods in which it is present coming in contact with metals must be taken into account, since stearic acid, as is well known, acts vigorously upon a whole series of metals.

There is one novelty which is worthy of note here: that is, the highly-oxidised castor-oil manufactured by a South German firm; with the aid of this it is possible in some cases to dispense with the use of the more expensive Besk mixtures and similar very adhesive ingredients. Sometimes the oil in question is heated with sulphur before being mixed with the rubber, but not to such an extent as to lead to the formation of substitutes.

The foregoing account cannot, of course, lay any claim to completeness, although the most important oily and waxy ingredients have been referred to. The authors are unfortunately not in a position to report upon the results of experiments with oils polymerised according to Axlerod's patent, which were stated on his part to be suitable for use in rubber mixings. In this process of polymerisation, as is well known, aluminium chloride is employed as the catalytic agent for effecting polymerisation. It may also be mentioned that Tung oil, polymerised by heat, has been recommended as a kind of substitute with the properties of a wax, but this product will not easily find general use, on account of its unpleasant smell.