a height of about 1 metre above the heater, where they remain while work is going on. The hood tapers away towards the top like a funnel, and opens into a pipe which leads to the exhauster. This pipe must not be too small in diameter. To the exit side of the exhauster a tube is attached which leads into the workshop and opens into a "Cyclone" dust-collector, which can either be stood on the ground or suspended. In this way the air is freed from the particles of sulphur. The air passes out through a side pipe, whilst the sulphur dust is compressed on to the walls of the cyclone, and is drawn off below into a receptacle.

As already mentioned, this method of vulcanisation is chiefly used for cut-sheet goods. Flat articles are simply laid in the sulphur bath and stirred about with a wooden stick; they are examined at frequent intervals; the larger articles are also frequently turned over, so that every part may be equally acted upon by the sulphur, and one side not become more highly vulcanised than the other.

The vulcanisation of teats, which have a curved surface, is carried out in the following way. The teats are taken off the moulds and stood in shallow iron trays, the depth of which is, however, a few centimetres greater than the length of the teats. The bottom of this tray is perforated with a large number of holes, each 5 to 7 mm. in diameter. Over each of these holes a teat is placed, and when all the teats have been placed in the tray, sulphur is poured over them. On cooling, the teats become firmly fixed to the iron sheet, do not fall out when the tray is inverted, and do not bend out of shape when the tray is immersed in the molten sulphur. In lowering the tray into the sulphur, the closed ends of the teats are put in first, the bottom of the tray last. The tendency of the teats to rise to the surface on account of their low specific gvavity, is checked by their pressure against the bottom of the tray, which keeps them in their original positions. The holes in the bottom of the tray allow the air in the teats to escape as they sink below the surface of the sulphur. When vulcanisation is completed the iron tray is carefully lifted out of the sulphur, whereupon the teats immediately rise to the surface, from which they are ladled off. They are then shaken up in a cloth, and well rubbed to prevent their sticking together, which they would otherwise do, thus causing difficulties in the subsequent treatment. The articles are now freed from adhering sulphur by heating in soda solution. Various other articles made from cut-sheet—urinals, for example—can also be vulcanised on sheet-iron moulds. In this case the small end of the mould must be put downwards into the sulphur, otherwise the article would leave the mould and rise to the surface.

This method of vulcanisation, in addition to being used for cut-sheet goods, is also specially suitable for soft or hard-rubber goods which have to be vulcanised in moulds, and particularly for bulk-production. The moulds are generally suspended from iron rods laid across the tops of the heating-vessels.

In this process the waste of time involved in the opening and closing of the heater, which is necessary in vulcanisation by means of steam, is done away with; and secondly, one has not to wait until the requisite number of moulds to fill a heater are ready before beginning the cure, but a single rod of moulds can be suspended in the sulphur as soon as it is ready, and the process repeated until the bath is full. By careful management it is possible so to arrange things that the first rod of moulds is fully vulcanised, and can be removed from the bath as soon as the last rod has been provided with moulds. With the same number of moulds it is possible by this method to vulcanise 40 per cent. more articles in a given time than by heating in steam. A further advantage possessed by these goods over steam-cured goods is that they exhibit a velvety coating on the surface, and that they are much more easily detached from the iron moulds than goods of the same qualities vulcanised in steam.

It is of great importance in the sulphur-bath process to keep the sulphur constantly at the right temperature; fluctuations in temperature seriously detract from the usefulness of the method. As soon as the sulphur gets overheated it catches fire, in which event the heating-vessel should be immediately closed to the air by lowering the hood.

The scum which collects on the surface of the sulphur during use should be removed at intervals with the ladle; fresh sulphur must also be added from time to time, to make up for loss by evaporation. For this purpose ordinary flowers of sulphur may be used.

The bath should also be kept hot during the night, otherwise the sulphur would cool down too rapidly and solidify, which means great waste of time, for the cold sulphur can only be heated up very gradually.

Consideration of the Vulcanisation of Proofed Fabrics by the Cold and the Hot Processes respectively.—It may be repeated that two methods of vulcanisation have to be taken into consideration, namely, that carried out at high temperatures in which elementary sulphur is the vulcanising agent employed; and in the second place, that carried out at ordinary temperatures by means of chloride of sulphur. The former method can be applied quite generally, but is comparatively troublesome, and necessitates, in most instances, more or less complicated arrangements. On the other hand, vulcanisation by means of chloride of sulphur cannot be adopted generally, since it does not permit of articles of above a certain (comparatively small) thickness being vulcanised right through. In the case of very thin sheet-rubber, however, its employment offers advantages which render its continued use in rubber manufacture a certainty, although the view is often held that cold-cured goods are not as durable as others. This view is not, however, correct in a general sense, even though goods which when vulcanised by heat have turned out perfect may not give satisfactory results on cold vulcanisation. The cause of the failure is to be sought, in this instance, not in the method, but in the conditions under which it is applied, such, for example, as the use in the mixing of ingredients with which chloride of sulphur does not agree.

When price and output have to be considered, cold vulcanisation offers very special advantages in the case of certain materials, and it cannot fail to be of interest to bring forward a few important points which very often remain unobserved, and lead to bad results. The most important point to be borne in mind in connection with the cold process is the great reactivity of chloride of sulphur towards other substances than rubber. Mixings which contain red-lead, litharge, zinc oxide or calcium hydrate, must remain absolutely out of the question as far as cold vulcanisation is concerned, for they are bound to give bad results under all circumstances.

The interaction between sulphur chloride and rubber proceeds quantitatively even when comparatively large proportions of chloride of sulphur—far exceeding actual requirements—are used. The rate at which the addition of chloride of sulphur to rubber takes place depends, however, entirely upon the concentration of the sulphur chloride.

Vulcanisation by means of pure chloride of sulphur in the liquid form is therefore not possible in practice. It would result in the conversion of the whole of the rubber coating into the horny chlorosulphide ($C_{10}H_{16}S_2Cl_2$), and in the consequent total destruction of the rubber.

On the other hand, in vulcanisation by means of the pure chloride in the form of vapour this danger is entirely avoided, but only the surface of the rubber is cured, the vapour not penetrating to the inner layers. The only remaining method is that involving the use of chloride of sulphur in solution, and this is the one in most general use. The suitability of a given solvent for purposes of vulcanisation depends upon its fulfilling the following conditions:—

1. The solvent must be chemically indifferent towards chloride of sulphur.
2. Its boiling-point should not be above 100° C.
3. It should have a constant boiling-point.
4. It should be a good solvent for rubber.

The first of these conditions is an obvious one, and the second is quite comprehensible, if it be remembered that the process of cold vulcanisation is a continuous one. With reference to the third condition, the vulcanising liquor is contained in an open vessel, and must preserve a constant level; in the course of the day evaporation of the vulcanising solution occurs at the comparatively high temperature of the workshop, and if the solvent be not a simple substance, but a mixture of different compounds with different boiling-points, evaporation takes place chiefly amongst the lower boiling portions of the solvent. This in itself would be of no importance, but in most cases it will lead to a more or less considerable change in the surface tension of the solution, generally in the direction of an increase. The result of this is that a larger quantity of the solution is transferred, by the roller revolving in it, to a unit area of the surface of the material. This results in a harder vulcanisation than was anticipated, and may go so far as to actually damage the article which is being cured. This happens when petroleum-ether is used as a solvent for the chloride of sulphur. In some large-scale experiments having for their object the introduction of this solvent in place of carbon bisulphide, signs of over-vulcanisation became evident after a short interval, and gradually grew more pronounced. The reason of this is not the increasing concentration of the vulcanising liquor (of course this also takes place in a simple solvent, but is easily compensated for), but the increase in surface tension which accompanies the rise in boiling-point.

The fourth condition is capable of an equally simple explanation; it has its basis in the fact that in consequence of the high velocity of the reaction between chloride of sulphur and rubber it is a very difficult matter to vulcanise a piece of rubber uniformly right through. Now the velocity of reaction is very much diminished by the presence of the solvent and diluent, and therefore, if the solvent fulfils the fourth condition, the solution of chloride of sulphur will penetrate into the rubber at a greater speed than that with which interaction between the chloride of sulphur and the rubber takes place at the surface of the latter, so that uniform vulcanisation right through the layer of rubber is dependent upon the suitable dilution of the chloride of sulphur. If, however, the boiling-point of the solvent be too low, it evaporates too rapidly, and only a relatively slight penetration of the layer of rubber can take place. In addition to this the speed of the reaction between rubber and chloride is increased to such a degree by the rapidly increasing concentration which occurs when such a solvent is used, that uniform vulcanisation can no longer be expected. A solvent with a very low boiling-point, and which therefore evaporates very rapidly, produces a more or less considerable fall in the temperature of the surface from which it is evaporating, inevitably resulting in the deposition of moisture upon it if the air is at all moist. Owing to this deposition of moisture a decomposition of the chloride of sulphur goes on side by side with the vulcanising action. This decomposition is not, however, of the simple kind it is ordinarily assumed to be. It is a fact that if the action occurs on a piece of rubber, and the products of decomposition are not at once removed, evil-smelling products are formed, which are very difficult to get rid of afterwards; care must therefore be taken to rigorously exclude all moisture. That carbon bisulphide is still not the most suitable of diluents is indubitably clear from the foregoing remarks; it has, however, been found, generally, that no other solvent, such, for example, as benzine, benzole, or petroleum spirit, is equal to it. Carbon tetrachloride is at present too costly to be considered, benzine has not a constant boiling-point, and has not sufficient penetrating power, the result of which is that the inner layers do not get cured. Benzole could only be used in its purest form as a diluent for chloride of sulphur, but its price is then too high, and it causes the rubber to swell up too much.

In making up the vulcanising liquor care must be taken to see that the chloride of sulphur and the carbon bisulphide are free from water, since water decomposes the chloride, forming hydrochloric acid and setting sulphur free. The percentage of chloride of sulphur is regulated according to the rubber mixing used, the thickness of the rubber, and the kind of raw rubber employed. Strictly speaking, pure rubber mixings should require a stronger liquor than those containing a high proportion of fillers. Different solutions need not, however, be made up for the better qualities, provided the same brands of raw rubber are used, for a material proofed with pure rubber solution takes up appreciably more of the liquor from the roller than others which are loaded with mineral ingredients, this being due to the fact that the pure rubber swells up to a greater extent and also more quickly. The proofed material is in contact with the liquor for only a very short time, and during this time takes up as much as its content of pure rubber will allow, and that is clearly proportionately less with lower qualities.

In the following table are recorded the results of experiments made with different raw rubbers, both alone and when mixed with substitutes and other fillers.

RESULTS OF VULCANISATION.

Nature of the Mixing used for Proofing.	Vulcanising Liquor.				
	1 : 40	1 : 34	1 : 30	1 : 20	Elasticity.
Pure Para	tacky	soft	good	hard	5
,, Ceara	soft	good	firm	brittle	4·65
,, Madagascar	sticky	tacky	soft	good	3·6
,, Mozambique	soft	pretty good	good	hard	4·4
,, Kassai	sticky	tacky	good	brittle	4·7
,, Congo	very sticky	pretty good	firm	cracked	4·4
,, Cameroon	very sticky	good	hard	...	1·8
Para with substitute	...	tacky	...	good	4·4
Ceara ,, ,,	soft	...	pretty good	firm	4·0
Congo ,, ,,	...	sticky	soft	good	3·8
Para with 20 per cent. other ingredients	soft	good	hard	brittle	3·0
Ceara with 20 per cent. other ingredients.	almost good	firm	cracked	brittle	1·7
Congo with 20 per cent. other ingredients.	almost good	good	bad	brittle	1·9
Para with 10 per cent. substitute and 20 per cent. other ingredients.	soft	too flabby	almost good	stiff	2·9
Ceara with 10 per cent. substitute and 20 per cent. other ingredients.	soft	good	firm	hard	2·0
Congo with 10 per cent. substitute and 20 per cent. other ingredients.	soft	good	brittle	...	2·1
Congo with 50 per cent. other ingredients.	soft	good	firm to hard	cracked	3·5
Columbian with 50 per cent. other ingredients.	...	...	...	...	3·9
Para with 50 per cent. other ingredients	good	brittle	hard	...	4·0
Cameroon with 50 per cent. other ingredients.	good	hard	...	...	1·7
Congo with 10 per cent. of Pontianac added.	brittle	...	...	...	...

If too dilute a vulcanising liquor be employed tacky products are obtained, which in course of time, often even in a few hours, decompose.

Results of J. Minder's Experiments on Cold Vulcanisation.—Sample pieces of rubber were vulcanised in liquor of the strengths indicated in the following table, and were then heated in steam under a pressure of three atmospheres for the length of time indicated.

The symbols used in the table have the following significance: — good, ○ tacky, | soft, × brittle, and ▬ hard.

Strength of Liquor.	Hours.											
	½	1	1½	2	2½	3	3½	4	4½	5	5½	6
1 : 100	—	○	|	|	|	|	|	|	|	|	|	|
2 : 100	—	—	○	|	|	|	|	|	|	|	|	|
3 : 100	—	—	—	○	|	|	|	|	|	|	×	×
4 : 100	—	—	—	—	○	|	|	|	|	×	×	×
5 : 100	—	—	—	—	○	|	|	|	×	×	×	×
6 : 100	—	—	—	—	—	○	|	×	×	×	×	×
7 : 100	—	—	—	—	—	—	○	×	×	×	×	▬
8 : 100	—	—	—	—	—	○	×	×	×	×	▬	▬
9 : 100	—	—	—	—	○	×	×	×	×	▬	▬	▬
10 : 100	—	—	—	○	×	×	×	×	▬	▬	▬	▬
11 : 100	—	○	×	×	×	×	×	▬	▬	▬	▬	▬
12 : 100	—	○	×	×	×	▬	▬	▬	▬	▬	▬	▬

When we come to consider more closely the vulcanisation of doubled fabrics, cold vulcanisation has to give way to the hot process. As already mentioned, doubled waterproof cloth consists of upper- and under-cloth. The latter takes the place of the lining. Both cloths are proofed, the upper one so as to be quite waterproof, while the under one is only coated to such a thickness as will enable it to stick well. In carrying out the vulcanisation the rubber coating of the upper-cloth is vulcanised, and then united with the unvulcanised under-cloth on the doubling calenders. The solvent has not undergone such complete evaporation at this stage as to interfere with the adhesive properties of the rubber coating, and, on the other hand, the process of vulcanisation is not complete before the two cloths are doubled together, so that a perfect union of them is effected between the rollers.

The vulcanising liquor is transferred to the under-cloth to a sufficient extent for both cloths to become thoroughly vulcanised. It would not be correct to vulcanise both cloths first and then double them together, since the under-cloth has not a waterproof coating, and the liquor would penetrate through the thin adhesive layer of rubber to the cloth, and might spoil the colour and give rise to spots. One great drawback to cold-cured doubled cloths is the "rustling" and the lack of suppleness in the feel of the finished stuff.

It is not practicable to vulcanise coloured cloths in steam, since they are considerably damaged in the process. The most satisfactory method of vulcanisation for these materials is by means of hot air in vulcanising stoves. Hot-air vulcanisation on drums in jacketed heaters is not to be thought of, for it must be remembered that the cloth is an exceedingly poor conductor of heat, and when it is wrapped round a drum to a considerable thickness, it is only the innermost layers, next the sheet-iron drum, and the outermost layers, which become vulcanised, or these become more highly vulcanised than the intermediate layers; for as soon as equilibrium of pressure is reached in these intermediate layers, all hot-air circulation is at an end. To get over this difficulty it would be necessary to interpose a sheet of tinfoil, equal in length to the cloth between the layers, as is done in America, so as to conduct the heat into the body of the stuff, and so bring about uniform vulcanisation of the whole length. Little benefit would result from the introduction of hot air under pressure into the stove, for the cloth is a bad conductor, and once the air-pressure becomes equalised throughout, things come to a standstill again.

The best method of vulcanisation involves the use of heating chambers, of which the internal arrangements are similar to those illustrated in fig. 40; the proofed doubled cloth passes direct from the spreading machine or calenders (fig. 41), through the heating chamber, which is kept supplied with hot air, and in which the air is kept in continual circulation. In this way an absolutely uniform vulcanisation can be effected; the chamber is completely enclosed, and the cloth in passing through it makes a number of convolutions, which can be increased or decreased at will according to the length of cure required by the rubber; the time of cure is the time which elapses between the entry of the cloth into the chamber and its exit, the temperature being that of the hot air.

Waterproof fabrics, coated on one side only, and on the inner surface of which higher demands are made, are best cured by the cold process, since it is not so easy, and indeed frequently almost impossible, to ornament the proofed surface when the goods are cured by the hot-air process; moreover, the number of ornamenting agents that can be used is smaller, and it may, indeed, be said that a given process of ornamentation gives incomparably finer effects with the cold cure than with the hot. The simplest method of imparting to the rubber surface a pleasing appearance consists, unquestionably, in spreading as thin a layer of rubber as possible, and using perfectly transparent solution without, therefore, any pigmentary substances. The pattern of the cloth, toned down by the colour of the rubber, is then visible through the transparent layer of rubber, to which the well-known "velvet" finish has been given before vulcanisation, by means of starch. Very good results are obtained by this process when cold vulcanisation is employed, particularly on cloths with floral or fancy designs. By the use of dyes soluble in benzole any desired colour can be given to the rubber, modified, of course, by the colour of the cloth underneath. The use of this process is, however, conditional on the employment of cold vulcanisation, for apart from the difficulty of preserving the transparency of the rubber-layer when it is vulcanised by heat, the colourings produced would be destroyed, almost without exception, by the hot process. One process for the ornamentation of proofings must be regarded as particularly successful; this depends upon the action of chloride of sulphur on the coating of starch covering the tacky layer of rubber. The mode of operation is based upon the observation that chloride of sulphur converts the powdery coating of starch into a semi-transparent layer with a silky gloss, and upon the further fact that whilst a double treatment of the rubber coating to be vulcanised with a 3 per cent. or a 2 per cent. solution of chloride of sulphur is equivalent to a single vulcanisation with a 5·5 per cent. solution, the starch is in the former case much more transparent than in the latter. In fact, the 5 per cent. solution has not a much greater effect upon the starch than the 3 per cent. solution, and the result is practically the same if the first solution is a 4 per cent. and the second a 1½ per cent., or conversely; this behaviour is utilised for purposes of ornamentation in the following manner:—

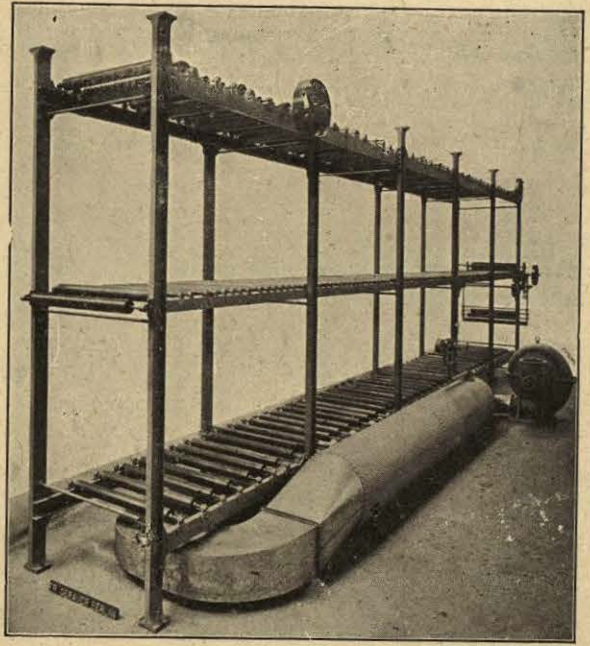

FIG. 40.

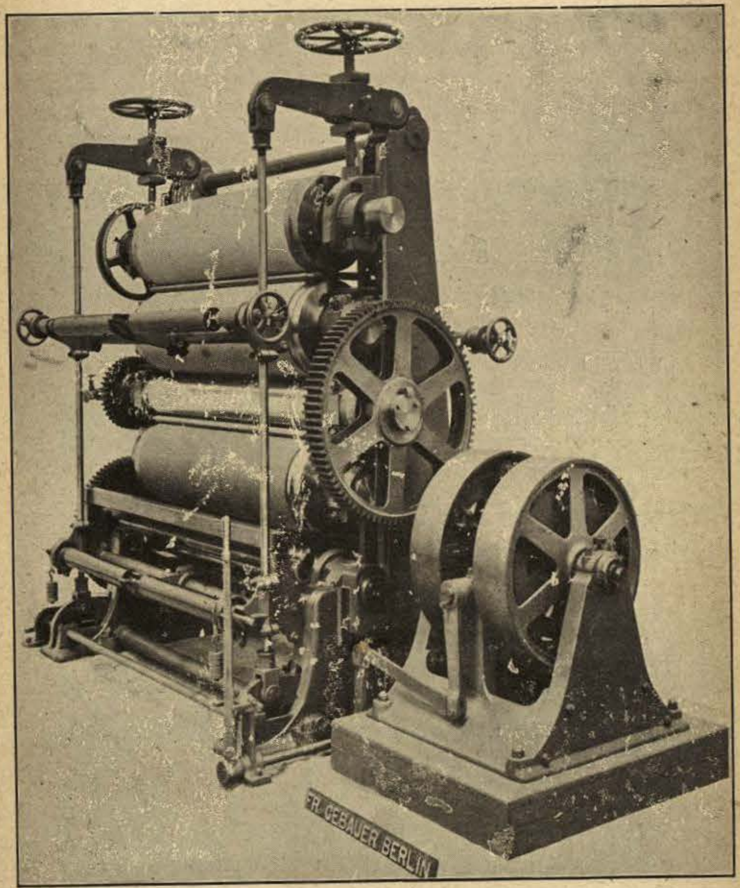

FIG. 41.

The rubber-coated material is first treated with potato starch,