that which does not adhere being carefully removed by means of a brushing machine. The rubber is then vulcanised by means of a 3 per cent. solution of chloride of sulphur, passing on to a second vulcanising machine in which a 1½ per cent. solution is employed. The vulcanising roller of this, however, is not smooth like that of the first, but is turned down to a depth of about 1 cm. in those places where it is desired that the liquor should not be carried up by it. These grooves are arranged in regular groupings with respect to breadth and axial distance, and the vulcanising liquor is therefore taken up from the roller in the form of bands, in this method of working. The result is that wherever the rubber has been in contact with chloride of sulphur twice, the starch becomes much more transparent than in those places which have been only once wetted by the liquor. The surface is therefore much less glossy in the latter places than in the former, which are almost transparent and colourless, but have a fine silky gloss. The most diverse effects can be produced in this way, and can be heightened and modified by the use of rubbers coloured by suitable pigments. The only difficulty in connection with this method lies in the circumstance that up to the present it has not been found possible to produce other than striped patterns, since the vulcanising liquor will not be carried up properly by engraved or elaborately turned rollers. A very good effect is, however, produced by cutting the bands on the vulcanising roller narrow, and very slightly waved axially. This roller is then used for the first vulcanisation. For the second vulcanisation, on the other hand, a roller is used which is also provided with narrow bands, but slightly inclined to the axis of the roller; in this way a highly satisfactory "moiré" effect is produced.

The cold vulcanisation process is particularly well adapted to the production of coloured effects, since delicate colours can be employed which would be destroyed by hot vulcanisation. In particular, oil-soluble aniline and resinate colours may be used. The lakes of coal-tar dyes are particularly well adapted for this purpose. Great circumspection is necessary in the selection of these, since many of them are not fast to water. The lakes of the polysulphuretted azo-dyestuffs in particular are defective in this respect, as are also those of the croceïns. The lakes of the basic dyes give good results as regards fastness to water, as sulphonated colour bases; also the amido-azo colours. The most suitable base for these lakes is a molecular mixture of aluminium hydrate and barium sulphate, obtained by precipitating aluminium sulphate with soda and with barium chloride. The basic colours are fixed upon this base with tannin and tartar emetic; the acid dyestuffs are mixed with soda solution and precipitated at the boil with the requisite amount of barium chloride, a solution of aluminium sulphate being then added until precipitation of the dyestuff is complete. The lakes must in every instance be washed quite free from soluble salts. In preparing rubber mixings with these lakes special care must be taken that all the materials used are absolutely dry, so that, as far as possible, the formation of hydrochloric acid within the rubber on cold vulcanisation may be prevented. The chances of damage to the shade of colour as the result of such formation of hydrochloric acid are certainly not very great, although this depends very much, of course, upon the nature of the particular coal-tar dye which was used in the preparation of the lake. But even the smallest production of hydrochloric acid is sufficient to entirely destroy the fastness of the colour towards water.

If it be desired to print in colour on the rubber surface, one may adopt the method given in Frankenburg and Weber's English patent, according to which the still tacky surface is dusted over with finely-powdered oxycellulose, the printing being done on this coating. Pigment colours (lakes) thickened with rubber solution are used, and most beautiful effects can thus be produced.

In selecting colour-lakes for rubber printing, the same points must be borne in mind as in selecting them for colouring the rubber mass, and reference may therefore be made to what has been said on that subject. But, in addition, it is of great importance that the covering-power of the colours used for rubber printing should be as great as possible. This condition is naturally best fulfilled by the mineral pigments, whereas all lake pigments have a tendency to transparency; this depends, however, upon their method of preparation, and especially upon the base used. If the printing is to be done on a white rubber surface instead of a coloured one, the case is, however, quite different, for then it is this transparency of the pigment which is its desirable quality, since it imparts to the print a brilliancy which cannot be attained by means of opaque colours.

In the waterproof industry some attention has also been given to the bronze-colour printing which has developed in recent years; indeed, more than in the calico-printing industry itself. The employment of this kind of printing is also conditional upon the use of cold vulcanisation in the case of all colours other than silver-white. Even the latter can only be cured by heat if it has been printed with aluminium, and then the silvery lustre suffers considerably, doubtless on account of the presence of foreign metals even in the purest commercial aluminium.

In printing with bronzes, however, one important fact must be borne in mind; the ordinary coloured bronzes consist actually of alloys which always contain tin and frequently contain copper. The destructive action of copper on cold-cured rubber is well known, and the danger lying therein is augmented by the unavoidable action of the chloride of sulphur upon the copper during the process of vulcanisation. Non-recognition of this fact will result in considerable loss, for in the course of time the rubber in all the places covered by the copper-containing bronze becomes completely destroyed by oxidation, the waterproof material being perforated in these places right through to the fabric. Even tin alloys, which are frequently used, are not absolutely free from suspicion, for it is a well-known fact that tin bronzes, free from copper, give rise to an action quite similar to that occurring with copper. In every case examined the rubber coating proved to be comparatively highly vulcanised: in other words, too strong a solution of chloride of sulphur was employed; this appears to lead to the formation of haloids of tin, which have an oxidising action on the rubber. These difficulties can all be avoided by restricting oneself to the use of pure or tinted aluminium bronzes, which, in addition to their safety, are possessed of a much greater brilliancy than tin bronzes.

In conclusion, we may refer to the influences to which the starch is exposed if the chloride of sulphur is diluted. The starch adhering to the surface of the rubber is exposed in a high degree to the action of the vulcanising agent, and it is here that the property of retaining water, possessed by starch, comes in, a property which is a very undesirable one from the present point of view. Air-dried potato starch contains, on an average, as much as 20 per cent. of water, and it is evident that the presence of this must result in the decomposition of a considerable proportion of the sulphur chloride taken up by the rubber, a circumstance which is, in fact, responsible for the evil smell of the waterproof. This can be almost entirely avoided by using benzole as a solvent, and by employing only well-dried starch, still warm. The material must then be vulcanised immediately the starch is put on, and it is best to carry out the two operations consecutively on a combined machine. If, on the other hand, carbon bisulphide be used as solvent, the advantages gained by the use of well-dried starch, and of the combined powdering and vulcanising machine, are nullified by the deposition

of moisture on the surface, caused by the rapid evaporation of the solvent and the consequent great decomposition of chloride of sulphur which occurs on the moisture-laden starch. The hydrochloric acid set free in this decomposition often dextrinises the starch to such an extent that the material acquires an unpleasant black surface in place of the well-known velvety gloss.

The simplest method of getting rid of the unpleasant smell of cold-vulcanised materials is to let them run for a few hours through an airing apparatus in which air, heated to a temperature of about 70° C., is driven past them, removing the smell.

After-treatment of cold-cured waterproof with ammonia is of doubtful value, since certain impurities in the ammonia tend to make the smell worse. If it be possible, the cold-cured material

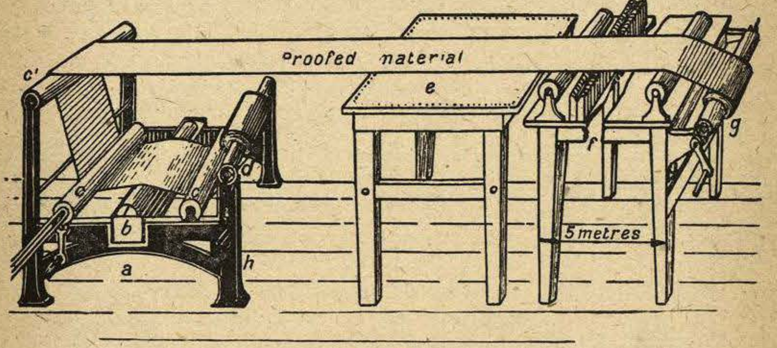

FIG. 42.

may be powdered with carbonate of magnesia, which absorbs the residual acid, and takes away the unpleasant odour.

The Cold-Vulcanising Shop.—This shop is situated in a separate building, primarily on account of the great risk of fire. The construction should be such that the building is provided with a double floor; the upper one, which is best formed of perforated iron-plates, stands about 1½ metres above the lower one, which is bricked or concreted, and on the ground-level. The space between the floors can be completely opened by means of valves, so that a current of air can pass through and carry away the vapours which descend through the upper perforated floor. The side-walls should have large windows all round, provided with glass jalousies, to ensure a vigorous circulation of air.

The most suitable machine for the cold-vulcanisation of waterproof cloth, reproduced in fig. 42, is very simple in its action. In the lead-covered frame *a* rests the solid wooden trough *b*, containing the beechwood roller, which revolves easily in two conical bearings.

Fig. 43 shows the wooden roller and trough in section. This wooden roller is one of the details in the process which is most worthy of attention; it must be turned so as to be absolutely true and perfectly smooth, and must under no circumstances become warped while in use; to this end special care must be exercised in the selection of a suitable piece of wood from which to make it. If the wooden roller gets warped, uneven vulcanisation will be the result, and spots and streaks will often be found on the finished article. The guide rollers over which the material is led are seen (*c c*) in fig. 44. The rollers *c'* are fitted into fixed bearings, while roller *c* runs in two movable levers, which make it possible to set the roller to any desired position, as shown in fig. 44. The object of this piece of apparatus is as follows:—A length of cloth is solutioned, on the spreading-machine, to each end of the material to be

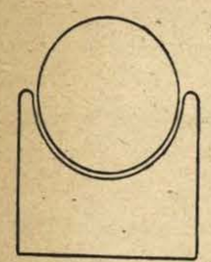

Fig. 43.

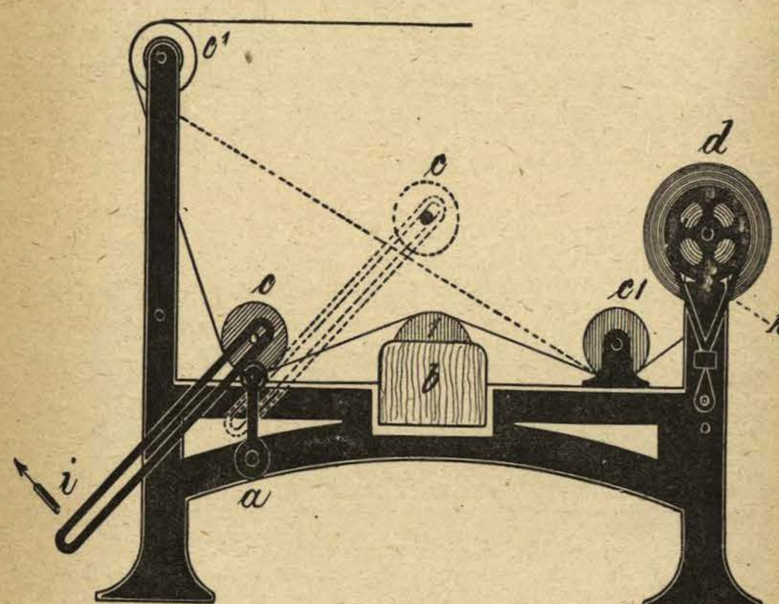

Fig. 44.

proofed. After proofing, the material passes, together with these end-cloths, on to the vulcanising machine, where it is rolled up as at *d*, figs. 42 and 44. The first end-cloth is passed under roller *c'*, over the vulcanising roller, then under *c* in slotted lever *i*, round *c'* over the heating-chest *e* and table *f* to roller *g*, on which it is rolled up until the join between the proofed and unproofed

cloths comes over the vulcanising roller 1. Lever *i* is then depressed by means of the handle *a* (fig. 44); this brings the proofed cloth on to the roller, and the vulcanisation can be started. When the other end of the proofed cloth, where it joins the other end-cloth, has passed the roller, lever *i* is raised. The final auxiliary cloth thus passes right above roller 1 and is not moistened by the vulcanising liquor, which would soon lead to its destruction. The roller *c* slides along lever *i* when the handle is raised or lowered, the lever being slotted. The two levers are connected by an iron bar, on which the handle is fitted. *e* is a heating-chest designed to hasten the evaporation of the solvent of the chloride of sulphur. *f* is an ordinary wooden table about 6 metres long, provided at each end with a guide roller, to prevent, as far as possible, rubbing of the material.

Just behind the front guide roller is an arrangement for discharging the electricity. This consists of two strips of wood (fig. 45), between which is clamped a copper-strip on to which a number of needles, with their points upwards, are soldered. The copper strip is connected, by means of insulated wire soldered to it, with a water tank outside. The needles are set with their points just below the level of the rounded edges of the wood, so as not to damage the cloth passing over them. At *g* (fig. 42) the proofed material is rolled up. The machine is belt-driven. An alternative construction of the machine is that in which a heating drum, 1 metre in diameter, is used instead of the heating chest. For the purpose of powdering the surface of the material, either before or after vulcanising, with potato-, rice- or maize-flour, a brushing apparatus is fixed behind the machine *a*, or else by itself; this is power-driven also, and by means of it the material is powdered with the flour and finely brushed. This method of powdering is employed in the case of the so-called electric-finished goods and single-proofed paletot-cloths.

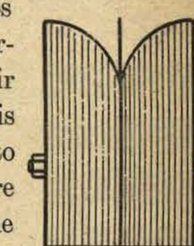

Fig. 45.

To return to the vulcanising process. Particular care must be taken to see that roller 1, in figs. 42 and 44, is clean. It should be rubbed dry with a cloth, because hydrochloric acid is formed upon it and must be immediately wiped off. When dry the roller is rubbed down with fine emery cloth, and then once again with a dry cloth. Before starting operations the trough *b* should also be carefully wiped out, the roller 1 being taken out for the purpose, and afterwards replaced so that it will revolve easily in its bearings.

At each end of the vulcanising roller a brass centre is let in, and into this the pointed brass screw projects. The screws are adjusted so that the roller runs easily: porcelain rollers and troughs have latterly come into use in place of wooden ones. When everything is in readiness the vulcanising liquor is poured into trough *b*, and vulcanisation now proceeds automatically in the manner depicted above. The material travels faster as it gets wound up on roller *g*, since the circumference of the roll is continually increasing; this is, however, an unimportant point; the rubber cannot be over-vulcanised by the quantity of solution taken up by the rapidly-revolving roller 1, for though on the one hand the roller takes up more solution the faster it revolves, yet, on the other hand, the time of contact between rubber and roller becomes continually shorter and shorter, and the net result is the same as at the original speed. The proofed material is uniformly vulcanised, and not, as is often thought, cured harder at the end. It may happen, however, that on account of the material running too slowly over the roller, the latter does not revolve fast enough to carry up the requisite amount of solution; the rubber is then under-cured, a result to be avoided. Should the roller not run with sufficient ease in its bearings, or should the centre of the roller not coincide with the centre of the wooden block out of which it was turned, the cloth will drag over the roll here and there, and in these places the rubber will be less highly vulcanised. One then wonders why the proofed material is good and bad in patches, the explanation being that given above. If the roller is turned from a cross-grained wooden block and has warped, the cloth will not make good contact with the hollows, and will take up too much liquor. The same thing will occur round the edges of the humps, too much solution being taken up where the material is not in close contact with the roller. These places become yellow, wrinkled, and hard. Now and again it happens that the vapours given off in the cold-vulcanisation process catch fire, owing to electric sparking between the cloth and some conductor or other. The material is electrified by friction, and if the potential difference is sufficiently great, the discharge takes place in the form of electric sparks. To prevent this firing, the apparatus already described is fitted up, a similar piece being placed behind the vulcanising trough. Should a fire occur in spite of these precautions, the cloth should be lifted away from the roller by raising the lever, and water should be slowly poured into the trough. The cloth is meanwhile rapidly run on, and not cut off. The flame burns low with a blue colour, and a pungent smell of sulphur dioxide

is given off. Material which is to be proofed on one side only is run over the vulcanising roller once; material proofed on both sides has to make two such journeys. Doubled stuff is generally vulcanised and doubled on the calenders (fig. 46). It is not necessary, however, to vulcanise both the cloths which are to be doubled together, as is often done. When two cloths are proofed for doubling, only one of them has a waterproof coat, this being the smoother of the two, while the other has only just sufficient rubber spread on it to make it adhere well. The first of these two cloths is vulcanised, the second not; for when they are carefully doubled

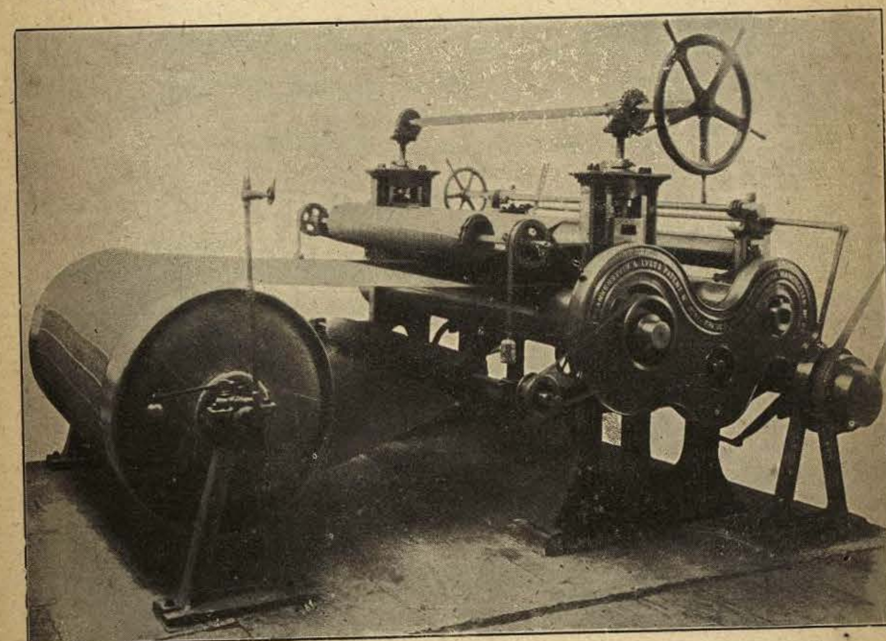

Fig. 46.

the lightly-proofed material is vulcanised when it comes in contact with that having the thicker coating of rubber. Fig. 47 shows diagramatically an arrangement for simultaneously vulcanising and doubling the proofed material. *a a* are the insulated cast-steel rolls, *b* is the vulcanising trough already described, *c c* the rollers upon which the cloth to be vulcanised and the lightly-proofed cloth respectively are rolled up, *d* also a wooden roller upon which the finished material is rolled up. After vulcanisation the material is hung up in a well-ventilated room to dry off.

The injuriousness of the vapours of chloride of sulphur and of carbon bisulphide is well known, and attempts have therefore been made to completely enclose the machines, and then to carry away the vapours by means of fans. This arrangement is to be preferred. Fig. 48 shows how the enclosing of the vulcanising machine in the shop may be accomplished. The door and lid *b* are open for the

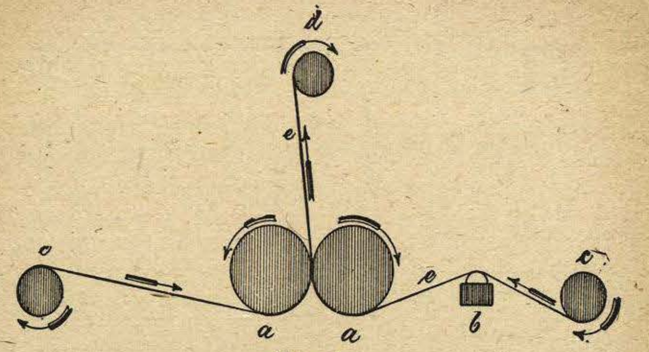

Fig. 47.

purpose of introducing the cloth; while the machine is in operation they are closed. *d* is a window to admit light into the chamber; through this the material can be watched, a condition which is absolutely necessary. *i* is the steam pipe leading to the heating

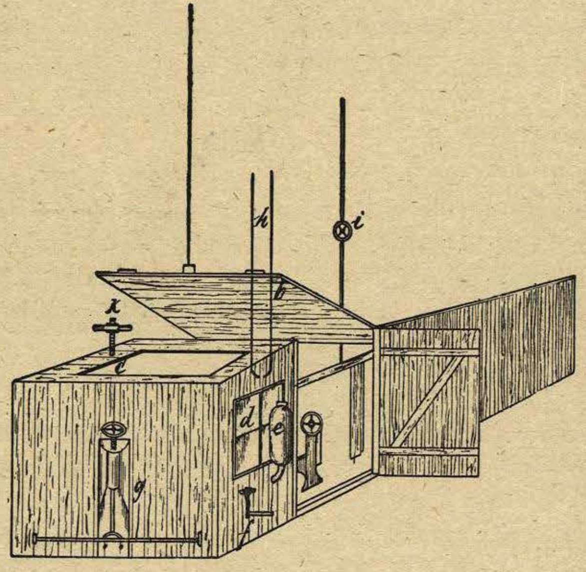

Fig. 48.

chest *e* of fig. 42. Before starting, the trough is filled as usual, and also the vessel *e* (fig. 49), the purpose of which is to replace the liquor in the trough automatically as it is used up. If the cloth gets creased, the lid *c* is opened, the hand is inserted through the opening, and the creases can then be easily smoothed out. The proofed cloth must obviously be braked in such a way as to cause

it to run under an even tension. In order to render this operation possible from outside the enclosure the brake *g* is provided. Vulcanisation with this arrangement is a pleasant process, in so far as that the poisonous vapours can scarcely be detected. The door and the lid *b* are closed while the work is going on. Air passes into the chamber through the opening *e*, and very little vapour can therefore escape. In fig. 49 the automatic arrangement for keeping up a constant level of liquor in the vulcanising trough is shown in diagram. *a* is an iron vessel, lead-lined, closed at *b* by means of an air-tight screw stopper. Tubes *e* and *c*, running side by side, lead from the vessel *a* into the vulcanising trough *f*, to a depth just below the level at which the liquor is to be kept. Tube *c* ends inside the vessel right at the top, whereas tube *e* only starts from the bottom. Vessel *a* is filled with vulcanising liquor through the opening *b*, which is closed again immediately after. On cock *d* being opened the solution now runs into the trough *f* until the level of the liquid rises just above the mouth of the tubes and closes them. When in the course of the vulcanising

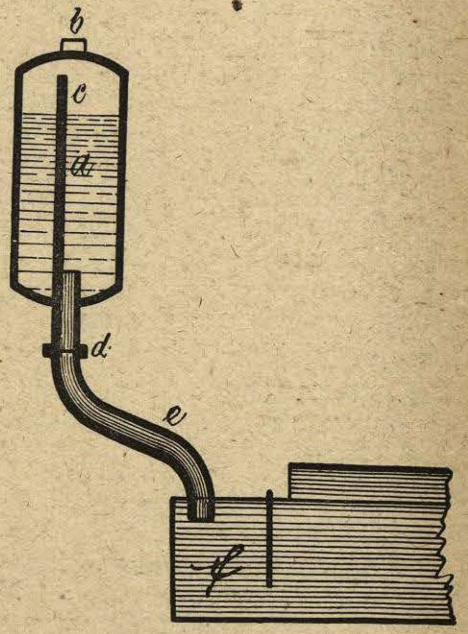

Fig. 49.

operation the level falls below the mouth of the tubes, more liquor flows from the vessel into the trough until the tubes are again closed by the rise in level, when the flow of liquor is checked; this goes on until, when work is finished, cock *d* is closed.

In addition to the room for vulcanising waterproof cloth, there are generally others for curing cut-sheet goods.

The ventilating pipe is usually fixed on the opposite side of the bench from that on which the workman stands; along the top of this runs a slot, through which the noxious vapours are drawn by means of a fan connected with the pipe. From the back wall of the vulcanising bench leading towards the rubber slot there rises a sloping hood which covers the whole of the bench with the dipping vessels on it filled with carbon bisulphide; as an additional protection to the worker, a narrow ledge of wood runs along the front upper edge of the cover. The dipper stands in front of the bench and dips the small cut-sheet articles, by means of a fork held in his left hand, into a vessel containing the chloride of sulphur solution, whilst two others, sitting down, prepare the articles for dipping by mounting each one upon a separate prong of the fork. This arrangement for vulcanisation, although it is to be preferred to the older measures adopted for the protection of the workman, has nevertheless its own particular weak points. In the first place, the continuous exhaust slot leads to an imperfect removal of the vapours. Secondly, the sloping cover, and in particular the outwardly inclined ledge at the top, are in the way, and the workers get into the habit of stooping down below them, and so manage to inhale harmful quantities of the noxious vapours. Thirdly, the vessels containing the liquor are merely stood upon the bench, and the draught is only a very poor one, because of the great difference between the sectional area of the outlet and that of the opening in front (which extends from the top of the bench to the bottom of the protecting ledge on the sloping hood); the result is that the vapours are not entirely prevented from diffusing out into the room. The strength of draught necessary must be arrived at by experiment. Again, the arrangement is incomplete, since it affords no protection to the workers sitting in front of the bench preparing the articles for dipping, against the vapours arising from the dipping forks as they are handed back to them. All these imperfections can fortunately be remedied by adopting the following solution of the problem. The dipping bench is on that side of the room where the windows are, in such a position that the dippers stand on both sides of it opposite one another. The female hands, who fill the balloons, etc., have all their arrangements fitted up on the opposite side of the room, along the back wall. The ventilating apparatus consists of two entirely separate systems, viz. that for the general ventilation of the room, which may supply warm air, and that for local ventilation at the working places. The general ventilating system, the main trunk of which is made of galvanised iron, and suspended at a height of about 4 metres above the floor, carries fresh air, drawn in by a large fan, through the six nozzles to the upper parts of the workroom. This air, which is drawn by the second localised system of ventilation direct to the working places, sinks down past the workers without being contaminated to any appreciable extent by the vapours. The nose-pipes are 24 cm. in diameter, and are arranged symmetrically in pairs; they pass the following quantities of air as determined by an anemometer:—

			Per minute.				
First pair	left-hand,	speed	300	metres, quantity	13·5	cub. metres;	
	right-hand,	,,	284	,,	,,	12·8	,, ,,
Second pair	left-hand,	,,	280	,,	,,	12·6	,, ,,
	right-hand,	,,	320	,,	,,	14·5	,, ,,
Third pair	left-hand,	,,	280	,,	,,	12·6	,, ,,
	right-hand,	,,	240	,,	,,	10·5	,, ,,

in all, a quantity of 4590 cubic metres of air per hour. Further ventilation through the windows in the roof or top-lights is not advisable, as it would interfere with the general circulation of the system.

The draught on the working bench, which is quite independent of the general ventilation, is induced by a fan through a flue running along the floor the whole length of the shop. The fan drives the air charged with bisulphide vapours through an underground channel into the vertical air purifier outside the shop. The dipping bench is provided with two series of dipping vessels, placed alternately one on either side of the exhaust pipe, at intervals of about 1·5 metres. Each vessel is sunk into a pocket in the bench, its upper edge being flush with the bench top. The pocket is a fixture, with the exception that the front of it is made in the form of a flap, which can be opened. The small exhaust opening, through which the pocket is connected with the exhaust pipe, is situated underneath the dipping vessel, so that a protective draught of air is set up round the vessel by the suction, and a favourable means provided for the escape of the heavy vapours of carbon bisulphide and chloride of sulphur from the lowest point of the pocket. The top edge of the pocket is surrounded on three sides by projecting, slightly-inclined ledges, an arrangement which constitutes a distinct improvement, leading to efficient working. The remainder of the bench surface, which occupies the space between two pockets, is filled up with a hollow inverted pyramidal opening, covered with perforated metal, the apex of the pyramid leading into the exhaust pipe. By this means the vapour given off and the drops of liquor which always get splashed about during the dipping process, as well as the vapours coming from the forks after they have been in the liquor, are drawn away direct through the perforated plate to the exhaust pipe, and only traces of vapour are left behind, to be carried by the air circulation into the exhaust shaft.