CHAPTER XI

CLOTHING AND PAPER

We shall now enquire into the nature of the substances used in the production of our clothing, and also into the several chemical processes that are entailed. Clothing is made of one or more of the following articles: wool, silk, fur, cotton, linen, leather, artificial silk and rubber. It is somewhat surprising that man should have chosen for his clothing many natural products which belong to the class, viz., proteins, that constitute a vital part of his diet. To this class belong wool, silk, fur and leather. Cotton and linen are essentially cellulose, a substance which, we have seen, cannot be digested by man. Rubber is essentially made of hydrocarbons, i.e., compounds of carbon and hydrogen alone, though sulphur is a necessary addition in order to impart to it wearing qualities. Artificial silk is a cellulose product prepared from either cotton or wood pulp.

The Protein Clothing Products.

(i) *Wool.*—The crude wool, as shorn from the sheep, contains many substances other than the protein, called keratin, that is actually the clothing material. These impurities are usually about 20% of the crude product, though they may occasionally be as much as 50% to 70%. The impurities are wool-fat or wax, suint, dirt and natural colouring matter. They are removed by a mechanical washing process, known as " scouring," in which the raw wool is subjected to the detergent action of one or more of the following substances : sodium hydroxide, sodium carbonate, soap, sodium silicate and ammonia. Valuable products are recovered from the waste scour-liquor.

The fat finds its way to the wool fibres through secretion by a duct which opens into the hair follicle. The suint is dried perspiration and contains potassium carbonate which may easily be extracted on washing. The dirt is generally adventitious and adheres to the wool fibre by means of the fat. This type of dirt separates from the fibre during scouring, though there is another kind of foreign matter, e.g., burrs, which become entangled in the fibres and cannot be disentangled in the scouring process. Another process is therefore rendered necessary. This process, which is known as " carbonisation," consists of soaking the wool in a dilute solution of hydrochloric or sulphuric acid, drying and then heating to 100° C. Such a treatment converts the vegetable cellulosic matter into a modified cellulose, hydrocellulose, which can then be pulverised and either blown or beaten out.

Reference may be made to some of the valuable substances manufactured from the impurities of crude wool. One is lanoline and known in pharmacy as *adeps lanæ*. Though sometimes spoken of as wool fat, it is not strictly a fat, as it consists mainly of cholesterol (see page 113). Lanoline is insoluble in water, but possesses a remarkable capacity for absorbing water. For this reason, it finds application in the dressing of skins. It is also used in "super-fatting" toilet soaps and in cosmetics and ointments. In some countries the potash present as carbonate in suint is recovered, though potassium salts can now be obtained as such prices as to render the recovery not economic.

(ii) *Silk.*—Closely allied with wool in regard to its chemical composition is silk. The protein constituents of silk are sericin and fibroin. These proteins are almost of the same chemical composition, but they differ considerably from a physical point of view. Fibroin is the constituent of the main filament, whereas sericin or "silk gum" forms the outer covering. Unlike most proteins, the silk proteins are devoid of the usual small amount of sulphur.

The synthesis of silk by the silkworm is yet another example of the wonderful performances that take place in the living being. It is during the larval, or silkworm, stage of the particular class of moths that the components of silk are made. The substances from which they are constructed are obtained from vegetable matter and appear in the form of viscous solutions in two silk glands, one on each side of the head of the larva. In order to spin its cocoon the silkworm ejects these solutions through very fine spinerets. On emerging, these solutions coagulate into filamentous structures and they are cemented together with a layer of sericin. Where the sericin comes from is by no means certain, though it is possible that, whilst the fibroin is secreted by the long tail-shaped portion of the silk gland, the sericin is secreted as a slimy fluid through the gland walls. One of the problems yet to be solved is why the honey-

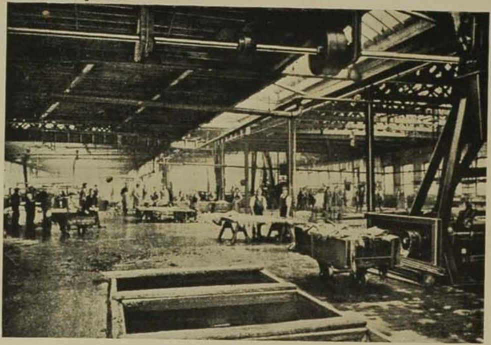

FIG. 23.—Leather Manufacture. Lime Yard.
(*Courtesy, Messrs. Wm. Walker & Sons, Ltd., Bolton, Lancs.*)

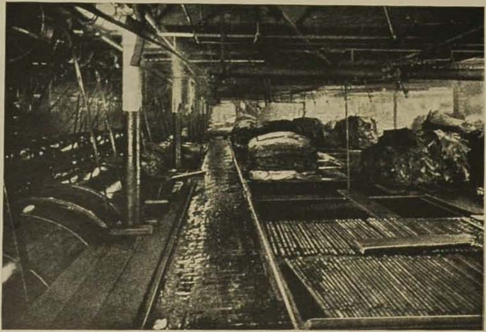

FIG. 24.—Leather Manufacture. Tan Yard.
(*Courtesy, Messrs. Wm. Walker & Sons, Ltd., Bolton, Lancs.*)

[*To face page* 164.

like fluid in the silk gland solidifies after being ejected. The coagulation sets in very soon after ejection, since the silkworm spins about a half a mile of silk filament continuously in making its cocoon, and there is no evidence of filaments sticking together as might be expected to occur if coagulation did not take place immediately. Moreover, if a mass of silk fibres adhered to one another it would be impossible to obtain the perfect silk threads available for the weaving of silken fabrics. Maybe the coagulation of the silk-solution is in some way akin to the clotting of blood.

The raw silk skeins are manufactured by heating a number of cocoons in water so as to soften the sericin. The ends are then joined together and the cocoons are simultaneously unwound. A number of individual filaments are twisted together to form composite threads and then wound on reels. Before these threads can be woven into fabric, they have to undergo further mechanical operations, including twisting a number of threads. Before these operations are carried out, the yarn is soaked in, or sprayed with, a fairly alkaline solution of soap containing a little oil. The oil appears to be required as a lubricant. This process is that of degumming, in which not only is some of the extraneous matter, but some combination takes place between the silk and the soda. Only traces of sericin are thus removed. Despite the protein nature of silk, it is remarkably resistant to the attack of moulds and bacteria.

(iii) *Leather.*—The skins of animals used in the manufacture of leather contain several proteins, but during the process of tanning many are eliminated, leaving behind the protein, collagen. This substance constitutes the basis of leather. It is a surprising fact that collagen and gelatine are almost identical with respect to their percentage composition of the elements of which they are made, viz., carbon, hydrogen, oxygen, nitrogen and sulphur. Moreover, collagen and gelatine are intimately related, for although collagen does not dissolve in water it will gradually become soluble on prolonged heating with water at 70° C. By so doing, the collagen becomes converted into gelatine, and as glue is actually crude gelatine, waste hides and skins form the starting material from which glue is made.

The chief stages in the manufacture of leather are : (1) *Preservation and disinfection of the skin.* (2) *Soaking and fleshing.* In this process the skins are prepared by removing all adhering flesh and fat. During soaking the proteins that are soluble in water are removed. These are the globulins. (3) *Unhairing and scudding.* The hair and epidermis are usually loosened by immersion in saturated solutions of slaked lime and then rubbed off. The lime treatment causes the skin to swell. (4) *Bating.* This process is necessary to remove the protein, elastin, comprising the fibrous matter. It is effected by the action of enzymes, e.g., pancreatin obtained from the pancreas of animals, in conjunction with ammonium chloride, which removes the lime from the skin. Formerly, bating consisted of immersing the skins in a warm infusion of the excreta of dogs, hens and pigeons. These infusions happen to contain the requisite enzymes, though the reason was, of course, quite unknown to the early tanners. The skin now assumes a "fallen" condition, i.e., it has become relaxed and flaccid. (5) Either *drenching* or *pickling.*

Drenching is practised if vegetable tanning is to be adopted, whilst pickling is preferable in the case of chrome-tanning. Drenching is a fermentation process in which the skin is placed in a liquor containing bran and allowed to undergo partial decomposition. Care must be taken to avoid this decomposition from proceeding too far, or the collagen may become attacked and a spongy leather result. Pickling comprises a treatment with a very dilute solution of sulphuric acid containing some common salt. (6) *Tanning.* In this process a substance which affords protection to the collagen against decomposition is deposited upon its surface. The substances ordinarily used are either tannins present in various vegetable extracts, or chromium oxide.

(*a*) *Vegetable Tanning.*—This method of tanning is very old, and it leads to leathers that are "full." In this country oak bark extracts find favour as they yield leather that is both firm and solid. In America hemlock bark is preferred for the manufacture of heavy leather. Other tannin extracts are those of quebracho, gambier, larch-bark and wattle-bark. For the leather to be used as the soles of footwear the tannins derived from the barks of the oak and chestnut are often used.

(*b*) *Chrome Tanning.*—This method of tanning dates from 1858 when Knapp showed that it was possible to tan leather by immersing it in a solution of chromium chloride to which a suitable amount of sodium hydroxide had been added. The process now adopted is essentially the same as that of Knapp. The protective layer of oxide of chromium is deposited on the collagen by the chrome liquor diffusing into the skin, entering into a chemical reaction with the skin protein and then precipitating the oxide. The chrome-tanned leather, in contrast with the vegetable tanned leather, lacks solidity. Fortunately this property can readily be imparted by immersion in molten grease or wax. The films of chromium oxide formed on the internal and external surfaces of the collagen of the skin are much harder than those of tannin and so imparts to chrome-tanned leather a greater durability. The wax and grease give water-proofness to the leather. Owing to its hardness chrome-leather is more difficult to manipulate by the boot operative. Chrome-leathers are finding increasing application in the uppers of the better-quality boots, in soles, harness, belting and hydraulic leathers.

(*c*) *Cellulose Clothing: Cotton, Linen, Rayon or Artificial Silk,* "*Acetate Silk.*"—The natural substances, cotton and linen, are chiefly cellulose. With the exception of acetate-silk, an example of which is sold as "Celanese," the artificial silks or rayons, as they are sometimes called, are made of regenerated cellulose, the initial cellulose having been derived from wood, paper or cotton or cotton linters.

(i) *Cotton.*—Cotton consists of about 95% of cellulose, and the remaining 5% is composed of alcohols that have a wax-like consistency. The length and fineness of the cotton fibres vary with the country in which the cotton plant is grown. Those suitable for spinning into yarn are on the average one and a half inches long. The linters which are very short and adhere as a fluffy covering to the cotton-seed can be removed by machine. These linters constitute one of the sources of cellulose for the manufacture of artificial silk, cinematograph films, celluloid, gun-cotton, etc. Among other uses the oil expressed from the cotton seed while hot is one of the chief ingredients of margarine.

As the cotton yarn is spun from millions of short fibres, it is clear that the resulting yarn is not as strong as would have been the case if the original fibres had been much longer. Thanks to the work of Mercer (1791 to 1866) cotton fabrics can be made stronger, given a silk-lustre and rendered more susceptible to dyeing. Mercerisation is effected by immersing the yarn or fabric in the stretched condition in a solution containing 18% to 25% of sodium hydroxide.

(ii) *Linen.*—Unlike cotton, linen is obtained from the stems of a plant, the flax-plant. Linen yarn contains more impurity than does cotton, being usually about 25%. Much of this is removed during bleaching with hypochlorites after the linen has been scoured with an alkaline solution. The fibres in the stems of the flax plant are held together by a gummy substance. This is removed by *retting*, which is a fermentative process caused by bacteria that live on the gummy matter and cause it to become soluble in water. The quality of the resulting linen is linked up with the bacterial actions that take place during retting, which are becoming better understood.

ARTIFICIAL SILK.

The history of the artificial silk is an excellent example of the development of a new industry as the direct outcome of scientific research. It seems that the idea of making " artificial silk-like threads " is very old, for we find that Hooke, in 1664, suggested that they might be made by " some ingenious person," and Reamar, in 1734, considered that certain varnishes which were unaffected by water and heat might prove of service. Schwabe applied to the Royal Society, in 1842, for financial assistance to enable him to carry out experiments that would " lead to the discovery of a substance which would form a homogeneous mass possessing the quality of ductility, and susceptible of being drawn out through fine holes, or otherwise into filaments or fibres possessing suitable strength and other properties to adapt it for manufacturing purposes." Shortly afterwards Andemars (1855) invented the artificial silk filament using nitro-cellulose, and in 1883 Sir J. W. Swan prepared denitrated nitro-cellulose filaments by squirting fine jets a nitro-cellulose solution into a bath. He did not, however, develop his invention and Count Hilaire de Chardonnet, in 1884, prepared the first artificial silk to be placed on the market. For this purpose he established a six million franc company at Besançon. Despeissis (1890) and Pauly (1892) later showed that artificial silk could be made from solutions of cellulose in ammonia and copper hydroxide—the so-called cuprammonium silk. The cellulose derivative, cellulose acetate, used in the manufacture of " acetate silk " of which Celanese is a familiar example, was first prepared in Germany, in 1865, by Schutzenberger. In 1894 Cross and Bevan in this country took out the first patent for its commercial preparation, and in the initial exploitation of cellulose acetate a considerable sum of money was lost, for although it gave satisfactory fibres, films and plastic masses, they became brittle on keeping. The original cellulose acetate dissolved readily in chloroform though it would not dissolve in acetone. In 1905, Miles discovered the method of preparing cellulose acetate which was insoluble in chloroform but which dissolved readily in acetone. Just by a slight variation in the method of preparation Miles was able to obtain a product with radically different properties and which are those necessary for the production of good "artificial silk" fibres. Since then, this method has been somewhat modified by numerous chemists, principally the Drs. H. and C. Dreyfus, who founded at Spondon, Derby, mainly by Government support, the British Cellulose Co. for the manufacture of cellulose acetate for aeroplane dope, and

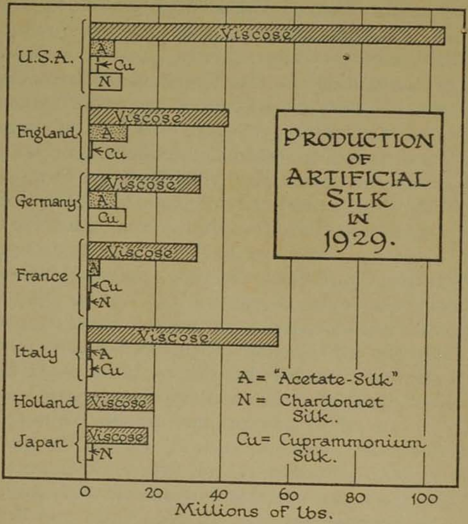

FIG. 25.

which now as the British Celanese Co. is manufacturing " acetate silk."

Another type of artificial silk, viz., *viscose*, was discovered, in 1892, by Cross, Bevan and Beadle. This type has been manufactured to a much greater extent than has anyone of the other three kinds. The dimensions of the artificial silk industry in the

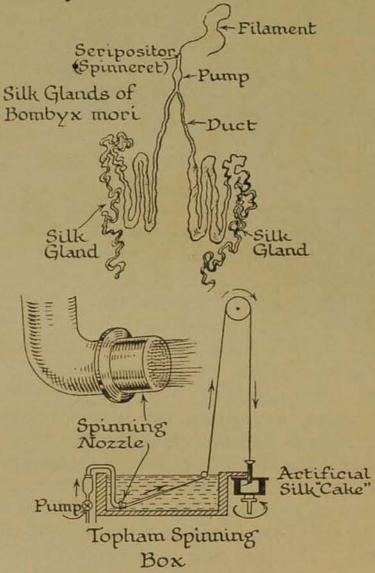

FIG. 26.—Production of Silk and Artificial Silk Filaments.

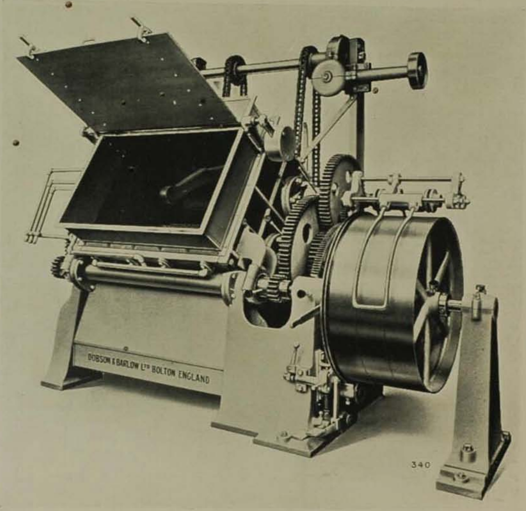

FIG. 27.—Manufacture of Artificial Silk. Kneading Machine.
(Courtesy, Messrs. Dobson & Barlow, Ltd., Bolton, Lancs.)

[*To face page* 172.

principal countries in 1929 will be seen from the chart on page 170. In 1929 the worlds output of artificial silk was 403,000,000 lbs., of which 80% was viscose, 8% acetate silk, 5% cuprammonium silk and 4% of Chardonnet silk. Thus it will be seen that the next rival to viscose is acetate silk. The latter has many properties that are superior to those of viscose. Whether acetate silk will ever be able to offer serious competition to viscose is a somewhat complicated problem. Thus viscose is made from wood pulp whilst acetate silk is made from a more expensive substance, viz., cotton waste and linters, and instead of requiring water as solvent as is the case with viscose, acetate silk requires expensive solvents such as acetone. Against this, acetate silk has a much greater covering power and is spun more quickly and much of the organic solvents may be recovered for further use.

To make either form of artificial silk the natural cellulose requires purification and bleaching, subjected to the attack of the appropriate chemical reagents, then dissolving in a suitable solvent and finally forcing through the fine holes or spinnerets of a nozzle such as that illustrated on page 171. Viscose and cuprammonium silk solutions on passing through these fine holes are coagulated into filaments through the action of another solution. A method of doing this is by using the Popham Spinning box shown on page 171. The wet cake is subsequently wound on hanks by a machine such as that on page 173. Chardonnet and acetate silk emerge from the spinnerets into the air where they assume solid form through the evaporation of the solvent. The former silk, however, is extremely inflammable on account of it containing groups derived from nitric acid.

Before the silk can be used it must be denitrated. The contrary is the case with acetate silk. It contains acetate groupings derived from acetic acid, which besides improving the strength of the fibres also tends to make them resistant to burning. Acetate silk is the only artificial silk which does not necessitate the decomposition of the cellulose compounds that must first be made to make spinning possible. Viscose involves the combination of the purified wood-pulp with sodium hydroxide and carbon disulphide, a foul smelling liquid prepared by heating charcoal with sulphur in a closed vessel. A viscous solution of this substance is forced through the spinnerets. The emerging filaments are attacked by sulphuric acid and are thus reconverted into cellulose. This process un-

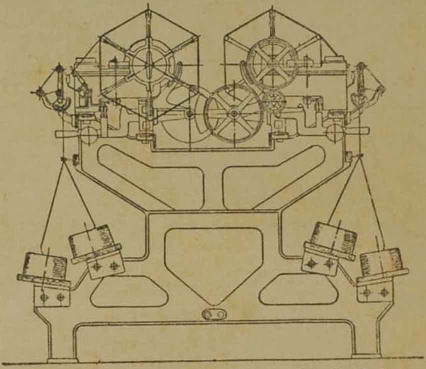

FIG. 28.—Artificial Silk Manufacture. Cake to Hank Reeling Machine.

doubtedly results in reducing the strength of the viscose filament. The cuprammonium cellulose filament is likewise regenerated into cellulose by acid treatment. The nitrate groups in Chardonnet silk are removed by immersing skeins of dry yarns in a solution of sodium hydrosulphide. It might be said that in the acetone solutions of cellulose acetate, from which the filaments are prepared, various chemicals are dissolved, the function of which is to increase the resiliency and durability of the fibres. As these plasticising agents are apt to melt when heated, e.g., during "ironing," it is necessary to exercise care not to apply irons that are too hot.

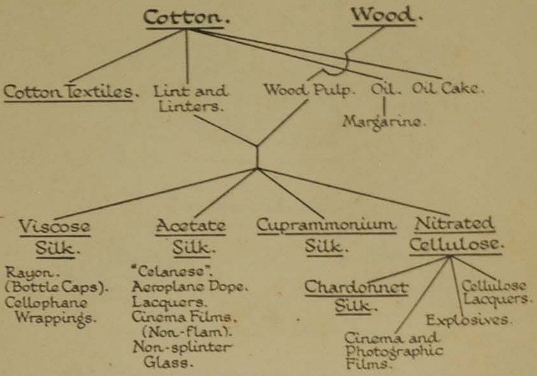

FIG. 29.

The regenerated cellulose silks, viscose, cuprammonium and Chardonnet, can in general, be dyed quite satisfactorily with the dyes used for cotton goods. This is not so with Celanese. The difficulty of securing suitable dyes for acetate silk was recently so great that the commercial development of this type of silk was long delayed. It has now been entirely overcome through the introduction of two new separate classes of dyestuffs by the British Dyestuffs Corporation, viz., the Ionamine dyes and the "Duranol" dyes. The introduction of the latter class is in the first place due to G. H. Ellis, who brought his knowledge of colloidal chemistry to bear on the subject.

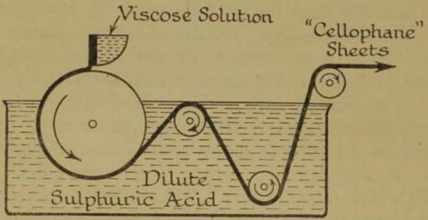

FIG. 30.—Manufacture of Cellophane Sheets.

TRANSPARENT WRAPPING MATERIALS.

Nowadays it is becoming the practice to wrap chocolate boxes, etc., with very thin transparent coverings. These may be made from either viscose or cellulose acetate by extruding a solution through a slit into one of sulphuric acid in the case of viscose or into the air in the case of the cellulose acetate solution. Particular care must be taken to remove any air bubbles from the solutions before extrusion by subjecting them to vacuum treatment. The above diagram illustrates the mode of preparing thin viscose sheets. After the sheet has passed through the first acid bath, it passes through a series of baths to ensure the removal of any impurities such as sulphur. After bleaching and washing, the sheet is passed through a solution of pure glycerine. A little glycerine is retained by the film, thereby giving it softness and pliability. The final treatment is one of drying by passing over hot rollers. One well-known variety of viscose wrapping sheet is marketed as Cellophane.

CINEMATOGRAPH FILMS, ETC.

Cinematograph films fall into two catagories: (*a*) nitro-cellulose, (*b*) cellulose acetate. Great care must be taken to produce films that are absolutely devoid of flaws or they may seriously interfere with the projected picture, and in this respect it is likely that nitrate films are more fool-proof than acetate films. Moreover the nitrate film is somewhat stronger than that of acetate, both when wet and when dry. Against this, nitrate film is highly inflammable whereas the acetate film is almost uninflammable. A less nitrated form of nitro-cellulose is known as celluloid or xylonite, and is used for making combs, toys, billiard balls, piano-keys, etc. Cellulose acetate is being put to similar uses, including that of electrical insulators. It should be mentioned that in either type of film appreciable amounts of plasticising agent are incorporated, camphor being perhaps the most common. Highly nitrated cellulose is used in the manufacture of explosives of the smokeless variety.

Aeroplane and airship dopes that are applied to linen fabric parts are made of solutions of cellulose acetate in acetone and other suitable solvents to which suitable softening agents have been added.

They are applied either by brushing or by spraying. Provided that the dope is applied in a dry atmosphere there will, on drying, be formed in the meshes of the fabric a continuous, adherent, transparent and protective film. Since the Great War solutions of cellulose nitrate and acetate, chiefly the former, have been used as lacquers in the decorating of wood and other surfaces on which a high polish is desired, e.g., on motor-cars. A familiar solvent used in nitro-cellulose lacquers is amyl acetate, which is characterised by the smell of " pear-drops." One of the difficulties experienced with these cellulose lacquers was their tendency to form non-adherent films, but through the greater choice of platicising agents now available and by the incorporation of certain natural gums this tendency has been almost entirely eliminated. A common softener is castor oil.

PAPER.

Like many of the artificial silks, paper is essentially cellulose, and like them can be manufactured from the same raw materials. They are rags, esparto, various kinds of straw, rags and coniferous woods, such as pine, spruce, poplar. When wood is the starting material, the bark is removed and the wood is cut up into very small chips. Their conversion into wood-pulp necessitates some process in which the non-cellulose matter is removed. They may either be boiled with sodium hydroxide solution under pressure and then treated with sodium sulphate, or be heated at 100° C. under pressure with calcium bisulphite liquors. When the raw cellulose has been sufficiently purified, it is beaten in water until the liquid assumes a milk-like consistency, any lumps being removed. To this liquid are then added sizing materials and "filling substances," e.g., china clay. Sizing is usually effected by means of solutions of alum and rosin dissolved in sodium hydroxide. These materials are taken up by the cellulose fibres. The liquid pulp is pumped over a horizontal wire mesh which, besides having a side-to-side motion, moves continuously onwards until the pulp-layer which has formed thereon is thrown on to a blanket that moves over a series of heated rollers. Emerging therefrom is a continuous sheet of paper, in which the fibres have been held together by the size and the desired surface has been produced by the fillers.