Platinum Alloys in the Production of Viscose Rayon

THE SELECTION OF MATERIALS FOR SPINNING JETS

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In 1884 Count Hilaire de Chardonnet patented a process for making artificial fibres by the extrusion of a solution of nitro-cellulose derived from mulberry leaves, the natural food of the silkworm. These were the first commercially successful man-made fibres, and the production of rayon by this method continued until the last nitro-cellulose factory was destroyed by fire in Brazil in 1949.

Other developments followed rapidly in the closing years of the last century. The cuprammonium process, which is still used to a small extent was patented in 1890, and the patents for the viscose process followed in 1891. In this process, cellulose—usually obtained from wood-pulp—is steeped in caustic soda, aged, and reacted with carbon bisulphide to give cellulose xanthate which is dissolved in caustic soda. The resulting viscose solution is then squirted into an acid bath where it coagulates as the cellulose is regenerated. The filaments so produced are soft and weak, but stretching them increases their strength, and after washing and drying they are ready for use.

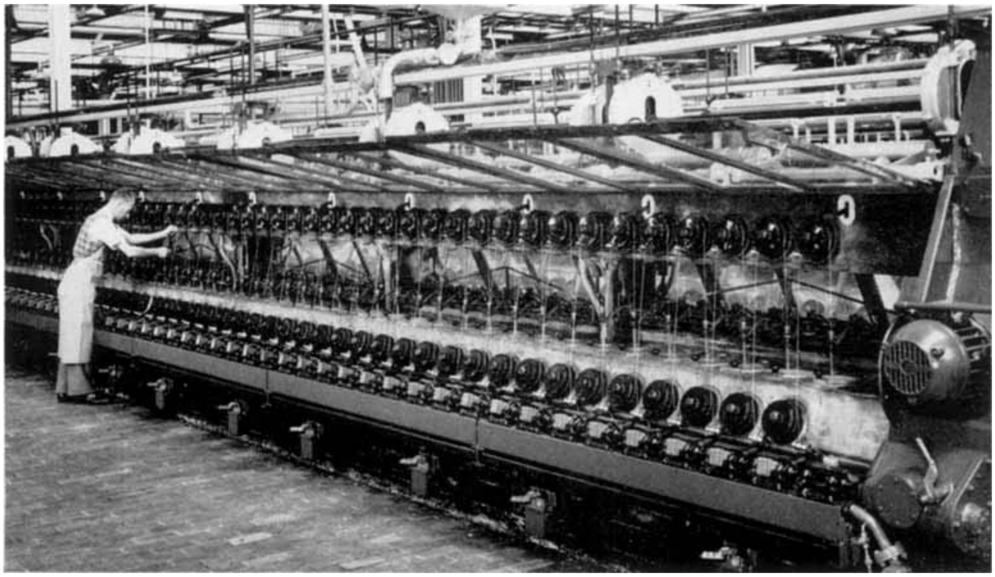
The production of viscose rayon was started in Britain in 1905 by Courtaulds. Initially it was an expensive fibre made as a continuous filament yarn which competed with silk. By 1920 world production was 33 million lb per annum, but the price was 200 pence per lb: twenty years later production had increased to 1,200 million lb per annum and the price had fallen to 33 pence per lb. Since then the world production of continuous filament yarn has doubled again.

The technical improvements in ordinary textile filament rayon during these forty years were marginal, but the versatility of viscose rayon was being exploited extensively in other directions. The production of staple fibre began in 1930, and by 1940 production was greater than that of continuous filament yarn. Diversification here included the making of fibres covering a wide range of lengths and thicknesses, so that they could be spun on cotton, wool, worsted, flax, jute and other spinning machinery. The addition of titanium dioxide could be used to dull the naturally bright appearance, and the introduction of pigments into the spinning solution gave fibres which could be blended into an infinite range of colours.

Another important development was the production of Tenasco—a strong industrial yarn—in 1935. By the end of the war, fibres of this type had almost completely replaced cotton in the big market for tyre-cords.

The years after the war were devoted to increasing the depleted production facilities. However, by 1953, improvements in the strength of rayon were needed to meet the threat of competition from nylon in tyre-cords. Fortunately earlier academic work had provided a basis on which to work.

Rayon is unique among man-made fibres in that its production is accompanied by a chemical reaction—the change from cellulose xanthate to cellulose. By varying the conditions under which the reaction proceeds, it is possible to vary the fine structure of the



Many thousands of platinum alloy spinning jets are in use in a modern viscose rayon plant. The illustration shows one unit engaged in spinning continuous filament in a Courtaulds factory

fibres. Ordinarily, rayon has a structure composed of separate skin and core. In the skin the texture of the arrangement of the long-chain molecules in crystalline and non-crystalline regions is finer than in the core, and by increasing the proportion of the skin structure, stronger fibres can be made. This and other improvements have resulted in a rise in the strength of rayon tyre-cords from 25 lb to 40 lb, and have succeeded in maintaining the price advantage of rayon over nylon in tyres.

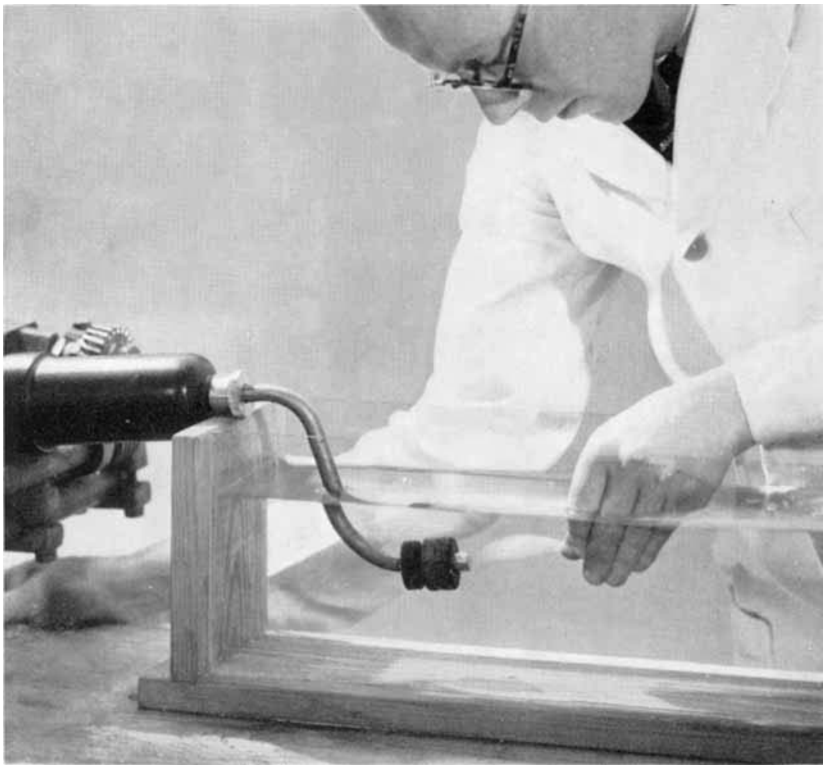
Similar developments are taking place, although more slowly, in textile rayons. All-skin fibres should have greater durability, and their round cross-section changes the appearance and reduces soiling. All-core fibres such as the so-called polynosic fibres have much better dimensional stability, especially on wetting. And fibres with an asymmetrical skin have a permanently built-in crimp. Other techniques give a collection of fancy yarns.

Viscose rayon is not really one type of fibre: it is a great variety of fibres which have a vast range of uses—dress-wear, furnishings, carpets, blankets, non-woven fabrics for interlinings, surgical swabs, filter fabrics, ropes, hose-pipes, conveyor belts—the list is too long to complete. Rayon is now second only to cotton in its scale of production and diversity of applications.

The Heart of the Process

The heart of the rayon production process is the spinning jet through which the viscose solution is extruded into the coagulating solution.

The compositions of these two solutions vary somewhat according to the particular type of viscose rayon being made, but a reasonably typical viscose would contain about 6.5 per cent of alkali in the form of sodium hydroxide and about 7.5 per cent of cellulose (present, of course, as the xanthate). The coagulating solution is essentially dilute sulphuric acid containing about 10 per cent by weight of the acid, together with about 20 per cent by weight of sodium sulphate and smaller amounts of zinc sulphate and glucose, the remainder being water. Thus the spinneret is subject on the one side to about



A simple demonstration of the formation of a multi-filament yarn by pumping viscose solution through the holes in a jet immersed in an acid bath (Courtaulds Ltd)

1.5 N sodium hydroxide and on the other to about 1.5 N sulphuric acid.

These are both severe conditions, which bring about chemical attack of most metals. The use of steels, for example, is immediately precluded for the manufacture of spinnerets for viscose rayon. In this respect, viscose differs from other manufactured fibres where steel spinnerets may be used.

Thus, for the manufacture of cellulose acetate filaments, the spinning solution consists simply of the acetate dissolved in either acetone or methylene chloride, both of which are without chemical action on steels. The solution is extruded into warm air, when the solvent evaporates, so again there is no corrosive action corresponding to that of the acid coagulating bath in viscose rayon manufacture.

A process more akin to viscose spinning is the manufacture of cuprammonium rayon. In this case a solution of cellulose in cuprammonium hydroxide is used, but although the final coagulation of the filaments requires an acidic bath they are first spun simply into water. Thus, the spinneret is not in direct contact with acid, and so may be fabricated from steel. Another difference between the cuprammonium and viscose processes which permits steel to be used for the former concerns the diameter of the holes in the spinneret. In the cuprammonium process this is of the order of 0.8 to 1.00 mm, whereas in a viscose spinneret the diameter may be as small as 0.03 mm, so that the removal of metal by corrosion is of greater significance.

Resistance to Chemical Action

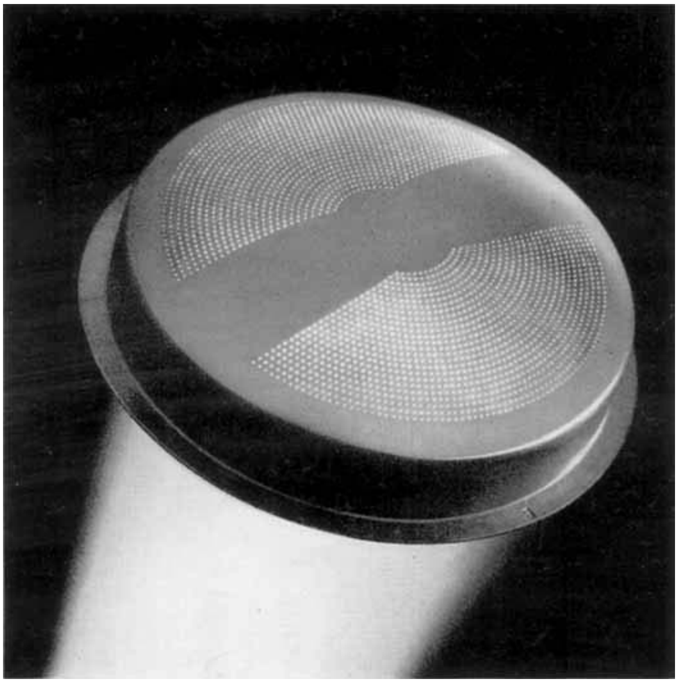
To return to the viscose process, we can see that spinnerets must be fashioned from materials that are capable of withstanding the simultaneous chemical action of 1.5 N caustic soda and 1.5 N sulphuric acid. So far as metals are concerned, this at once limits the choice to the noble metals, platinum and gold, and some of their alloys, and also tantalum protected by an oxide film.

Two alloys in particular have been widely used; 10 per cent rhodium-platinum and 30 per cent platinum-gold. The former, because of its higher cost, is normally restricted to use where the conditions are most exacting and the cheaper one is used where the conditions are less critical.

However, although such alloys will resist direct chemical attack by acid and by alkali, and on that account are suitable for spinneret manufacture, other factors also have to be taken into consideration. One of these, and one which mitigates against the use of any metal for spinneret manufacture, is the occurrence of electrochemical phenomena.

In the viscose process, one side of the spinneret is in contact with an alkaline solution and the other with an acid, and the two solutions form a junction inside the bore of the spinneret. If the spinneret itself is an electrical conductor (i.e. a metal), the system behaves as an electrical cell, most simply regarded as a form of hydrogen ion concentration cell. As with all concentration cells, the electrode in contact with the more concentrated solution will assume a positive charge, so that the spinneret becomes polarised, the surface in contact with the alkaline solution bearing a negative charge and that on the acid side a positive charge.

With steel spinnerets, of course, these electrochemical effects would in themselves cause corrosion, enhancing the deleterious effects of direct chemical attack. The noble metals are not corroded, but nevertheless a current will flow, resulting in electrolysis of the viscose solution passing through the jet. The most serious result is that the negatively charged xanthate ions will be attracted to the positive surface of the spinneret, where they will be discharged and decomposed, ultimately giving rise to a ring of cellulose blocking the jet. Some deposition of sulphur also occurs, but this may arise from the normal decomposition of the xanthate in the acid solution rather than electrolytically. The acid coagulating bath penetrates some distance



The number of holes and their pattern in a jet vary according to the type of rayon to be produced. This type of platinum-gold alloy jet has over 2,000 orifices and is made and used in the production of staple fibre by Courtaulds Ltd

Piercing, forming and polishing the holes in a spinning jet are intricate operations demanding considerable skill and accuracy. Here one of the operators in the Johnson Matthey jet production shop is broaching the holes in small rhodium-platinum alloy jets for spinning tyre-cord. The built-in binocular microscope is a feature of the instruments used to pierce and form the jet holes

up the jets, so that coagulation and the precipitation of insoluble solids actually begins in the jet. Thus, although noble metal jets are durable and represent a considerable improvement over steel, they are not entirely without disadvantages. Naturally, a great deal of effort has gone into devising ways of overcoming these defects. There have been two methods of approach: first to avoid the electrochemical effects which are responsible for deposition and blockage, and secondly to prevent deposition while allowing the electrolysis to continue.

One obvious method of avoiding electrical effects is to fabricate the spinneret from a non-conductor. The material must also withstand the direct attack of the alkaline and acidic solutions as well as possessing the requisite mechanical properties. Most attention seems to have been paid to the use of synthetic rubies, and ceramic spinnerets are also seriously considered. The major difficulties are probably connected with piercing these materials with the necessary precision. A similar method of approach is to coat the spinneret with a non-conductor, and silicone fluids are now being investigated for this purpose.

Another method of avoiding electrical effects is to neutralise the charges on the spinneret by passing a current in the opposite direction. A more satisfactory method is to make the spinneret as a whole carry a large charge relative to some other conductor in contact with the liquid. This is most easily done by using the lead lining of the coagulating bath as the second electrode —the cathode—and applying a potential of the order of 1 to 1.5 volts. In this way, choking of the jets can be prevented for periods of up to four weeks.

In practice, however, the most usual

method of avoiding deposition on the spinneret is by the addition of anti-fouling agents to the viscose solution before spinning. These are dispersing agents which serve to hold solid particles in solution during the short interval of time between the entry of the viscose into the spinneret and the formation of coagulated filaments.

Mechanical Properties

So far, only the chemical and electrical requirements of spinnerets have been considered, and we have seen that these can, in the main, be met by the use of noble metals. Finally, attention must be paid to the mechanical properties required of a satisfactory spinneret. For the production of good quality filaments the spinning jets must be made with great accuracy and possess a high surface finish and maximum durability. The accuracy required in the piercing of the holes demands a material which is completely uniform in structure, while the attainment of highly polished surfaces requires as small a grain size as possible. It is these two properties which the metallurgist must seek, allied with a convenient method of producing the necessary hardness to give durability.

The blank caps are normally produced from strip by conventional presses, and should at that stage be uniform in thickness and have a high surface polish, particularly on the inside face.

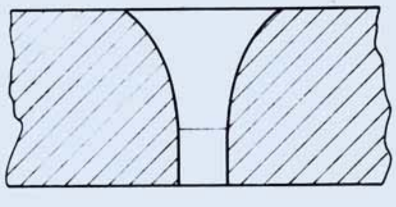
According to the metal used, piercing of the jets may be carried out with the metal in the hard or softened form. Piercing is naturally simpler with a soft cap, but can only be done this way if the pierced cap can subsequently be hardened without affecting the size and internal surface finish of the holes themselves.

The 10 per cent rhodium-platinum alloy, while possessing excellent resistance to corrosion, unfortunately has a relatively large grain size and this causes difficulties both in drawing and piercing and also in obtaining the necessary high polish. An alternative alloy having the same high corrosion resistance but a much smaller grain size is 3 per cent ruthenium-platinum. Piercing is simpler and the finished spinneret can be given a high polish.

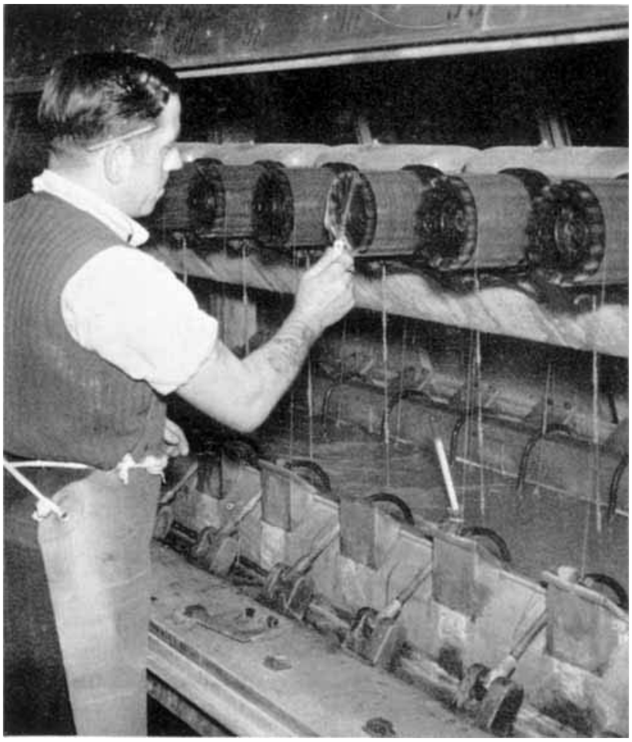
The widely used 30 per cent platinum-gold alloy presents little difficulty in working and will take a high polish. Traditionally the alloy has been rolled to a hardness of approximately 180 Vickers before pressing the caps, the holes then being pierced through the hard face. However, the addition of a small percentage of rhodium produces an alloy that can be worked to a fine-grained structure having a hardness of only about 120 Vickers. This is accomplished by a carefully controlled cycle of rolling, annealing and solution treatment. Caps are produced and pierced from this relatively soft material and then, by a suitable heat treatment, brought to a hardness of around 220. This process combines the simplification of piercing associated with the soft alloy with the desirable properties of the fully hardened form. Increasing the platinum content of the alloy to 35 per cent permits the manufacture of spinnerets with a final hardness of around 280 Vickers, while for special purposes alloys containing from 40 to 50 per cent platinum are also used.

The number of holes and their pattern in

The satisfactory performance of a spinning jet depends on the correct shape and accuracy of the holes, and great care must be taken to ensure both the smooth blending of the lead-in with the capillary and the sharpness of the junction with the outlet face



In addition the capillaries of each of several thousand orifices in one jet must all be of exactly the same length, while the orifices themselves must be highly polished and truly circular. Johnson Matthey jets are produced to meet these stringent requirements



Newly formed viscose rayon threads being led out of the coagulating bath on a textile-type continuous spinning machine in one of Courtaulds factories

the jet vary according to the type of rayon to be produced. Typical figures range from less than 100 holes per jet for textile rayon, from 650 to 1,500 for tyre-cords and to as high as 6,000 for staple manufacture. The shape of the holes is much the same for all types of rayon, and it is, indeed, of great importance if satisfactory filaments are to be obtained. The lead-in diameter is always somewhat greater than that of the major part of the orifice, and considerable care is needed to ensure completely smooth blending of the lead-in with the straight capillary. The maintenance of a sharp junction between the capillary and the outlet face is also a critical feature. To achieve this, the outer face is carefully polished after piercing, the holes themselves being filled with glass or some other material that can readily be removed by melting, in order to protect the polish of the jet walls from the abrasive. In jets produced by Johnson Matthey, for example, orifice diameters may be as small as 0.03 mm and are accurate to within $\pm$0.0015 mm on all diameters.

Although it is very likely that many new manufactured fibres will make their appearance, and even that existing fibres will be modified in various ways, the development of radically different spinning arrangements seems improbable. Drastic changes in the nature of spinnerets are therefore also unlikely, and it seems most probable that the main advances will be metallurgical, leading to alloys having even more desirable properties, both during manufacture and in use. There always remains the possibility of using non-conducting materials. Artificial gem-stones would be satisfactory if the difficulties of piercing them could be overcome. Another possibility, at present, perhaps more remote, lies in the use of a synthetic polymer. However, in spite of these possibilities, it seems likely that noble metal alloys will remain the only suitable materials for viscose rayon spinnerets for many years to come.