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SYNTHETIC FIBERS
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MAN-MADE FIBRES

R. W. MONCRIEFF

NEWNES-BUTTERWORTHS
LONDON BOSTON
Sydney Wellington Durban Toronto

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PREFACE

The nylons, the polyesters and the acrylics continue to dominate the fibres scene. Their growth has been, and continues to be, amazingly rapid; so rapid in fact that the production of cotton has had to be cut back by legislation in the U.S.A., and there are large unsold stocks of wool throughout the world. These two effects are undesirable, and it seems reasonable to think and hope that they will be only very temporary. Cotton and wool are two of our finest fibres, and the proper function of man-made fibres is to supplement, not to supplant, them. By early 1973 there had been some improvement in this respect.

With the world-wide increase in the production of synthetic fibres there has come a sharp fall in their prices, particularly in those of the polyesters, which can now be made much more cheaply than polyamides. This fall in prices is to be welcomed. Just as cheap rayon brought down the price of cotton in the 'fifties, so now we are seeing the cheap synthetic fibres bring down the price of wool. Synthetic fibres made from alpha amino-acids, fibres that we have awaited so long, have not yet come out in strength, but there seem to be two or three on the threshold, and their coming may augur a new era for man-made fibres. They are, in fact, overdue, but nevertheless they will find the going rough to begin with.

Increased fibre production has led also to a spate of improvements in the dyehouse, and activity in this department has never been so great. The new developments in dyeing are to be welcomed by all the textiles industry. The synthetic-fibres industry grows apace.

My thanks again to the manufacturers who have so generously supplied information and illustrations. I am particularly indebted to those who have given me a great deal of help with this the sixth edition. It is forty-odd years since I was doing some of the spade work in fibre stretching; it is 25 years since I wrote the first edition, and it is only with contemporary help that the usefulness of the book can be maintained.

Throughout the text of this book various words are used which are Registered Trade Names. These are indicated by being printed with an initial capital.

R. W. MONCRIEF

FUNDAMENTAL CONCEPTIONS

CHAPTER 1

ALL ordinary yarns, either man-made or natural, consist of a number of fibres or filaments. In the case of man-made fibres this number is usually in the range 15-100—*i.e.*, most yarns will be composed of not fewer than fifteen and not more than 100 filaments. If a single thread of a man-made fibre yarn is broken, the individual filaments will usually be observed to splay out. They can always be pulled apart mechanically. The reason this multi-filament construction is adopted is that it confers pliability and flexibility on the yarn; a yarn composed of a number of fine filaments is much more flexible than a solid, thick filament of the same diameter as the yarn. The use of a large number of very fine copper wires in ordinary lighting-flex may be recalled as an analogy. The purpose is exactly the same: to obtain flexibility.

Monofilis

For special purposes, monofilament yarns are made. One familiar application of this is when the monofilament is relatively thick and is used as bristle. Most readers will be familiar with the use of nylon bristle in tooth-brushes. Very strong synthetic fibres, such as nylon, are sometimes spun in very fine monofilis to give the sheerst of stockings, and such fine yarns of 7, 12 and 15 deniers are usually monofilis. They are made as monofilis to give durability because coarse filaments are less easily damaged than fine, and as the monofil is itself so thin it is sufficiently pliable to be knitted without difficulty. It is easier, too, to make a coarse single 15 denier filament than a multi-filament 15 denier yarn, and the prices of monofil 15 denier nylon, for example, are lower than those of 3 filament 15 denier (each filament being of 5 denier) nylon. This is illustrated in the figures on p. 1021. Sometimes, too, for special decorative or novelty effects, relatively thick monofilament yarns may be used, but the great majority of artificial-fibre yarns are spun in multi-filament form.

Continuous Filament

All the yarns that have just been discussed, multi-filament and monofil, are continuous filament yarns and are like real silk in the sense that the filaments are very long indeed, miles long in some

cases. They are glossy, lustrous and silky, and were the first kind of artificial silk. At first, all artificial silk was continuous filament—long almost endless filaments. Nowadays, less than one-half of the fibres that man makes are continuous.

Staple

Most of the other half of man-made fibres are discontinuous; they have been chopped up into short lengths of a few inches. In this way they have become more like cotton, which has a fibre length of about 1-1½ in., or wool, which is usually within the range of 3-6 in. fibre length. All man-made fibres are spun continuously, but more than half of their weight is chopped up into short lengths, usually of from 1 to 6 in. Often this cutting is done continuously as the filaments are made; the chopping up is part of the process. The chopped up fibre is called "staple fibre" and is used for spinning (p. 732) on the cotton and worsted systems, being very largely used for blending. The staple man-made fibre and a staple natural fibre are spun together as a blend. That way the mixing of the two fibres is very intimate. Blending or mixing of fibres should be done at as early a stage in manufacture as possible. Of such blends, that of polyester (Terylene) and wool is as well known as any. Such a blend could not be made from continuous filament fibre; only by using the chopped up staple of the man-made fibre does perfect blending with wool (or cotton or linen) become possible. Sometimes, perhaps most often, the man-made staple is spun on its own without the admixture of a natural fibre; spun rayon fabrics for frocks, curtains and underwear have been ubiquitous for twenty years. Continuous filament fibres are long fibres, often miles long, and an end is reached only at the end of a bobbin or other package, or if a thread accidentally breaks. Staple fibres are very short, nearly always just a few inches. Sometimes for special reasons fibres of different lengths, say of 1½ in. and 3 in., are mixed in staple, but this is unusual. Nearly always all the fibres in a bale of staple fibre are the same in length. Staple fibres are mixed up in random arrangement and have to be sorted out, made parallel to each other and twisted in old traditional textile operations to make them into yarns.

Tow

Tow is fibre that is spun with tens or hundreds of thousands of filaments bundled together into a loose rope and wound up on to some sort of spool or package. It is used for direct-spinning operations (p. 736 *et seq.*) in which the filaments are cut or broken at

intervals of a few inches and spun directly into yarn. Tow serves the same end as staple fibre, but the cutting into short fibres is done at a later stage. The disadvantage of staple fibre is that although the filaments are all spun parallel one to another, and although they end up parallel in the final yarn, in between they are mixed up, pointing in all directions. It seems wasteful to randomly parallel filaments and then sort them out and make them parallel once again. The use of tow avoids this; the filaments are spun parallel and are kept parallel right up to the finished yarn. Tow is often supplied in a rope of about 200,000 denier, say 40,000 filaments each of 5 denier.

Denier

The coarseness of a yarn or a filament is usually gauged as "denier". The denier was the unit used in the real-silk industry long before man-made fibres came. It is defined as follows:

Definition. The denier of a yarn (or filament) is the weight in grams of a length of 9,000 metres of that yarn (or filament).

If, for example, 9,000 metres of a yarn weigh 100 grams, the yarn is said to be 100 denier; if 9,000 metres of another yarn weigh 45 grams, that yarn is 45 denier; if 9,000 metres of a single filament weigh 3 grams, that filament is of 3 denier. An instrument very suitable for rapid determination of denier is the Torsion Denier Balance (Fig. 1). A 9-metre length of the yarn is run off on a wrap-reel, hung on the hook of the balance, the pointer turned approximately to the expected denier on the dial, the balance released, a final adjustment of the pointer made, and the denier of the yarn read directly.

Conversion Factor for Cotton Counts

Many readers may be more familiar with the use of cotton counts—*i.e.*, the number of hanks of 840 yd. which will weigh 1 lb.—and it is useful to have a factor by which cotton counts may rapidly be converted into denier and vice versa. This may be obtained in the following way:

Consider a yarn of 1 s cotton counts. What would its denier be? As the yarn is 1 s cotton counts 840 yd. weigh 1 lb.

or $840 \text{ metres weigh } 453.6 \times \frac{39.37}{36} \text{ grams}$

so $9,000 \text{ metres weigh } 453.6 \times \frac{39.37}{36} \times \frac{9,000}{840} \text{ grams}$
 $= 5,315 \text{ grams.}$

Hence the denier is 5,315.

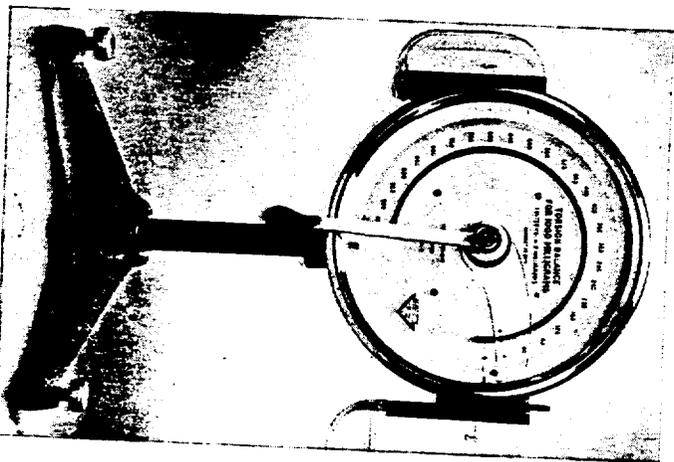
If the yarn is x s cotton counts, then 9,000 metres will weigh $\frac{5,315}{x}$ grams. Accordingly, to find the denier of a yarn from its cotton counts, divide 5,315 by the cotton counts. Conversely, to find the cotton counts of a yarn of known denier, divide 5,315 by the denier.

For example, 50 s cotton counts $\equiv \frac{5,315}{50}$ or 106 denier

2/60 s cotton counts $\equiv \frac{5,315}{30}$ or 177 denier

30 denier $\equiv \frac{5,315}{30}$ or 177 s cotton counts

150 denier $\equiv \frac{5,315}{150}$ or 35.4 s cotton counts



[White Electrical Instrument Co. Ltd., Malvern.]

Fig. 1.—Torsion Denier Balance.

Conversion Factor for Worsted Counts

Remembering that the basis of the worsted system of counts is the number of hanks of 560 yd. in 1 lb., the reader will find it easy to calculate that the conversion factor from worsted counts to denier is 7,972.

For example, 20 s worsted counts $\equiv \frac{7,972}{20}$ or 399 denier

200 denier $\equiv \frac{7,972}{200}$ or 40 s (nearly) worsted counts.

It will be noted that approximations have been made in these calculations. The reason for this is that counts and denier are slightly variable; there is no point in describing the denier of a yarn as 398.6 when even the average of batches of it will vary by ± 2 denier.

Uniformity of Denier

Yarns are not absolutely uniform in denier. They are nearly so, and uniformity is a very desirable characteristic. It is not unusual for a tolerance of ± 3 per cent to be allowed—*i.e.*, in a batch of 100 denier yarn, extremes of 97 and 103 deniers may be found.

Filament Denier

Yarns of the same denier may be spun with different numbers of filaments. A yarn of 100 denier may be produced with twenty filaments and also with sixty filaments. The former would have a filament denier of $\frac{100}{20}$ or 5, and this is relatively coarse, and would be found in cheap "bread-and-butter" viscose. The latter would have a filament denier of $\frac{100}{60}$ or 1.67, and would be a speciality yarn suitable for the manufacture of high-class materials. The more filaments there are in a yarn for a given denier, the more soft and supple it is. Very fine filament yarns are suitable for fabrics where draping, anti-crease properties and softness of handle are required. Such yarns are, however, more liable to abrasion than those of coarse filament yarns, and for purposes where hard wear is a *sine qua non* coarse filaments are to be preferred. Men's linings are, for example, harder wearing if made from coarse filament yarns. There are uses for both coarse and fine filament yarns.

Tex and Millitex

Another unit which is sometimes used instead of denier is the tex, which is defined as the weight in grams of 1,000 metres (instead of

9,000 metres used in the denier definition). The millitex is one-thousandth of the tex, so that one and the same filament could be described as 9 denier or 1 tex or 1,000 millitex whilst others could be 1 denier or 0.111 tex or 111 millitex; $4\frac{1}{2}$ denier or 0.5 tex or 500 millitex; 100 denier or 11.1 tex or 11,100 millitex; 90 s cotton counts or 59 denier or 6.6 tex.

Another way to look at it is that the tex of a yarn or filament is its weight in milligrams per metre. Sometimes the term decitex or dtex is encountered; its relation to the others is:

$$0.1 \text{ tex} = 1 \text{ d(eci)tex} = 100 \text{ millitex} = 0.9 \text{ denier}$$

The tex is a universal unit, used for all fibres: man-made, wool, cotton, etc. The terms tex (for tows) and decitex (for yarns and single filaments) have become more widely used, and, in those organisations which were originally chemical, tex and dtex have largely displaced the term denier. But in those organisations with a long textile and fibre tradition, denier is the term still mainly used. Possibly too, the desires of the Textile Institute have led to the wider use of the tex terms. There is much that is good and traditional in our fibres industries, and where possible it should be retained, especially in nomenclature. Perhaps we shall be able to talk about deniers for a long time yet. Whether is it more enlightening to speak of a 150/30 yarn (meaning 150 denier 30 fils) or of 167/30 (meaning 167 decitex 30 fils)? Both mean the same.

Twist

Nearly all yarns are twisted, as this protects the filaments from damage. Untwisted yarn is almost impossible to weave or knit without damage. The twist is expressed in turns per inch (t.p.i.).

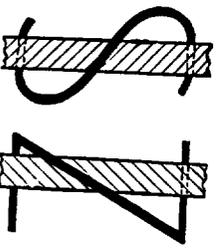


FIG. 2.—The two directions of twist. (Leonard Hill, Ltd.)

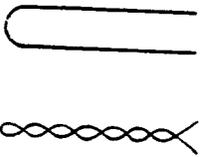


FIG. 3.—Balanced and unbalanced yarns. (Leonard Hill, Ltd.)

Direction of twist is described as "S" or "Z", the meaning of which will be clear from Fig. 2. This "S and Z" system is unambiguous,

and fortunately has almost universally replaced many other mutually conflicting systems. Sometimes, too, yarns are doubled or folded, and then the doubling or folding twist should be such that the yarn is balanced. Fig. 3 illustrates balanced and unbalanced yarns; the latter tend to twist if held in U form.

Fig. 4 shows a simple type of twist-tester. One end of the yarn is held in a clamp, the other end is rotated until a needle can be drawn from one end to the other through the untwisted filaments. The number of turns that has been required to untwist the yarn is read on the engraved dial. Stroking the filaments with the needle will often electrify them, cause them to balloon, and so simplify their separation.

The addition of twist always increases the denier of any fibre. For fairly low twists (up to say 30 t.p.i. for 70 denier) the increase in denier is not great, but at one point secondary twist develops (the

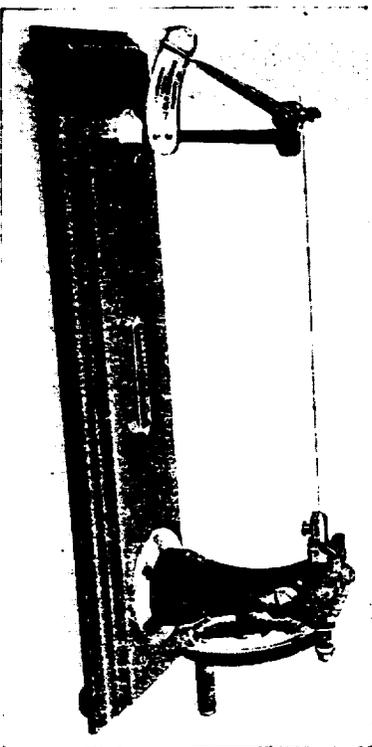


FIG. 4.—A twist-tester.

(Goodbrand & Co., Ltd.)

already twisted fibre starts to "corkscrew"), and then the denier rises quickly. This effect may be seen in the following table of figures for Dacron polyester yarn.

Initial denier of Dacron.	Denier with twist (t.p.i.) of									
	1.	8.	14.	24.	36.	48.	70.	100.		
40 (34 fils) :	40	40	40	40.5	41	42	44	49		
70 (34 fils) :	70	70	71	72	74	77	83	—		
210 (34 fils) :	210	213	216	226	246	271	—	—		

This behaviour is not peculiar to Dacron; all fibres behave somewhat similarly. As twist rises strength falls and elongation at break rises, as shown by the following figures for 210 denier 34 fils Dacron.

Twist (t.p.i.).	Tenacity (gm/denier) (see p. 11).	Elongation at break (per cent) (see p. 13).
1	7.1	11
23	6.6	15
36	5.3	16
47	3.9	17

Nomenclature

"Artificial silk" was the early name for all man-made fibres. When such fibres were first spun the avowed aim of the manufacturer was to make something that would replace real silk, and the name was then quite apposite. The description "artificial silk" is less appropriate to-day, as artificial fibres have long passed the stage of imitating real silk. New fibres have been produced which have properties entirely different from those of any natural fibre. Man-made fibres is the most usual description nowadays.

Rayon. The word "rayon" is now used universally to describe fibres made by the viscose and cuprammonium and acetate processes.

Whilst there are no hard-and-fast rules, the reader is advised to use the word "rayon" for fibres of cellulose origin (viscose, cuprammonium, and cellulose acetate), and the term "synthetic fibres" for the true synthetics, nylon, Vinyon, etc. All of them can be referred to collectively as "man-made fibres".

Viscose Rayon. One other point to note is that manufacturers always use the term "viscose rayon" for the fibres. They do not speak of the fibres as "viscose", but restrict this term to describe the solution from which the fibres are spun. Converters and merchants (in fact most people who do not manufacture it) often describe the fibre as "viscose", but, to be quite correct, the reader should refer to the fibre or yarn or fabric as "viscose rayon" and not as "viscose".

Azlon. The name "Azlon" has also been tentatively approved by the Federal Trade Commission as a generic term for reconstituted protein fibres, irrespective of the type of protein used as the base of the fibre. This term appeared to include soya-bean, casein, groundnut and zein fibres which comprise a group with diverse compositions and properties, but "Azlon" seems never to have become popular. Most of the Azlons have failed and been discontinued. Ardil (pea-nut protein) and Vicara (maize protein) were the best, but they are no longer made.

Acrylics and Modacrylics

In America, the Federal Trade Commission has defined rules for the enforcement of the federal Textile Fiber Products Identification Act (March, 1960). According to these, acrylic fibres are those that comprise at least 85 per cent of acrylonitrile. Modacrylics are those that contain from 35 to 85 per cent acrylonitrile. There are many acrylic fibres: Orlon, Acrilan, Courtelle, Creslan are typical. There are only four modacrylic fibres: Yarel, Dynel, Kanekalon and Teklan. "Spinning". It is unfortunate that the verb "to spin" and its derivatives are used in the following two quite different senses.

1. To spin viscose rayon, by extruding a viscose solution through a fine hole into a coagulating bath, or to extrude a solution of cellulose acetate in acetone through a fine hole into an air-drying medium, or to extrude a melt of nylon through a fine hole into a cooling atmosphere. All man-made fibres are "spun" in this way, just as a spider spins its web or a silkworm spins its cocoon. This always results in a continuous filament which may, however, immediately or later be cut into staple or short lengths.

2. To spin cotton fibres into a yarn by arranging them in parallel formation in a bundle and gradually pulling out and thinning the bundle and at the same time twisting it. A similar process is carried out on wool, mohair, flax, schappe, etc. Man-made fibres which have already been "spun" in the first sense (extruded) are sometimes then cut into staple fibre, and spun in the second sense, *i.e.*, parallelised, thinned and twisted into a yarn.

Both meanings are "to make a yarn", but in the first case it is from a solution or a melt, in the second it is from fibres. A staple fibre yarn has been "spun" in both senses of the word. No one who has worked amongst textiles will find confusion in the two meanings of the word "spinning", but it may well be confusing to the student.

Tenacity

The tenacity or strength of rayons is usually expressed as grams per denier. If a load of 250 grams will just break a 100-denier yarn, the tenacity is said to be 2.5 grams per denier. Some fibres such as the regenerated proteins have tenacities of the order of 1 gram per denier; others, like nylon and Fortisan, of 6-7 grams per denier.

Sometimes the tenacity or tensile strength is expressed in pounds per square inch instead of in grams per denier, and we can derive the relation between the two methods of expression as follows:

Suppose we have 1-denier filament of specific gravity 1, then its cross-sectional area will be:

$$\frac{1}{900,000} \text{ cm.}^2$$

because 9,000 m. or 900,000 cm. of it weigh 1 gram.

If the specific gravity of the filament is not 1 but 2, then the cross-sectional area of the 1-denier filament will be

$$\frac{1}{900,000 \times 2} \text{ cm.}^2$$

and if the specific gravity is d then the cross-sectional area of a 1 denier filament will be

$$\frac{1}{900,000d} \text{ cm.}^2$$

or

$$\frac{900,000d}{1} \times 2.54^2 \text{ in.}^2$$

This by definition has a breaking load of 1 gram, so that a "filament" 1 in.² in cross-sectional area would have a breaking load of:

$$\frac{900,000d}{900,000d} \times 2.54^2 \text{ grams, or}$$

$$\frac{453.6}{453.6} \text{ lb.}$$

or

$$12,800d \text{ lb.}$$

Accordingly to convert tenacity expressed as grams per denier into tensile strength expressed as lb./in.² we can use the expression

$$\text{Tensile strength} = (12,800d \times \text{gm./denier}) \text{ lb./in.}^2$$

Thus Courlene with a specific gravity of 0.92 and a tenacity of 2 grams per denier has a tensile strength of:

$$12,800 \times 0.92 \times 2 \text{ lb./in.}^2 \text{ or}$$

$$23,500 \text{ lb./in.}^2$$

Glass with a specific gravity of 2.54 and a tenacity of 6.3 grams per denier has a tensile strength of:

$$12,800 \times 2.54 \times 6.3 \text{ lb./in.}^2 \text{ or}$$

$$205,000 \text{ lb./in.}^2$$

It would need a load of about 90 tons to break a glass "filament" of 1 in.² section. Fortisan with a tenacity of 7 grams per denier and a specific gravity of 1.51 has a tensile strength of 136,000 lb./in.²; nylon with a tenacity of 5.5 grams per denier and a specific gravity of 1.14 has a tensile strength of 80,000 lb./in.²; cuprammonium rayon with a tenacity of 2 grams per denier and a specific gravity of 1.53 has a tensile strength of 39,000 lb./in.²

Although in engineering practice the terms "tenacity" and "tensile strength" are used synonymously, it is convenient in dealing with fibres to confine the expression "tenacity" to that property (cohesiveness) which is measured in grams per denier and "tensile strength" to that which is measured as lb./in.². There is the density factor that divides one from the other and two fibres with similar "tenacity" values may have very different "tensile strength" values; e.g., glass and nylon both have tenacity values of about 6 grams per denier but the tensile strength of glass (because it is more dense) is more than double that of nylon. Sometimes one encounters, instead of grams per denier, the term grams per decitex. Referring to p. 8 we see that 1 decitex = 0.9 denier, so that 1 gram per decitex = 1 gram per 0.9 denier, or 1.11 grams per denier. A fibre with a tenacity of 2.5 grams per denier has a similar tenacity of 2.25 grams per decitex. It savours a little of pedantry to those of us who have been brought up on deniers.

Elongation at Break

The elongation at break is an important characteristic of a yarn. If a length of 100 cm. of a yarn can be stretched to 112 cm. before it breaks, it is said to have an "elongation at break" or an "extension" of 12 per cent. Except for special purposes, such as tyre-cord, a minimum extension of 10 per cent is desirable to facilitate textile working. Ordinarily, there is no advantage in an extension being higher than 20 per cent. Often, in the manufacture of yarns, it is possible to make a yarn with either a high tenacity and a low elongation at break, or a moderate tenacity and a reasonably high elongation at break. As a rule, the manufacturer compromises, and produces a yarn that will have the highest strength compatible with an extension high enough not to give trouble in winding, weaving and knitting. Often two kinds of filament will be spun; a very high tenacity yarn with a fairly low extension intended for industrial use, and a yarn with a somewhat lower tenacity and higher extension and generally a softer handle for apparel use. As an example, Tergal, the French equivalent of Terrylene, is made by Société Rhodiacceta in high tenacity of 6.5 grams per denier with 10 per cent extension and also in normal filament with 5 grams per denier tenacity and 20 per cent extension. Rhodiacceta even make a third variety their staple fibre, which has a tenacity of only 3.5-4 grams per denier but an extension at break of 40-25 per cent. Such modifications are usually dependent on the degree of stretch that is applied to the fibre either during the actual spinning operation, or in the drawing

(stretching) operation that follows it, or in both. The greater the stretch, the higher the tenacity and the lower the extensibility. Stretches are usually quite high: 4 or 5 times the spun length is quite usual in some of the synthetic fibres and 10 or 12 times is not unknown. The natural fibres cannot be stretched much and it is the ability of man-made fibres to take high stretches in the plastic state that enables fibre manufacturers to make yarns with surprisingly good physical properties.

The conditions under which tenacity and extension are measured must be kept standard. An instrument very suitable for making determinations is Goodbrand's Single Thread Tester shown in Fig. 5. Fibres should be conditioned (p. 22) before test.

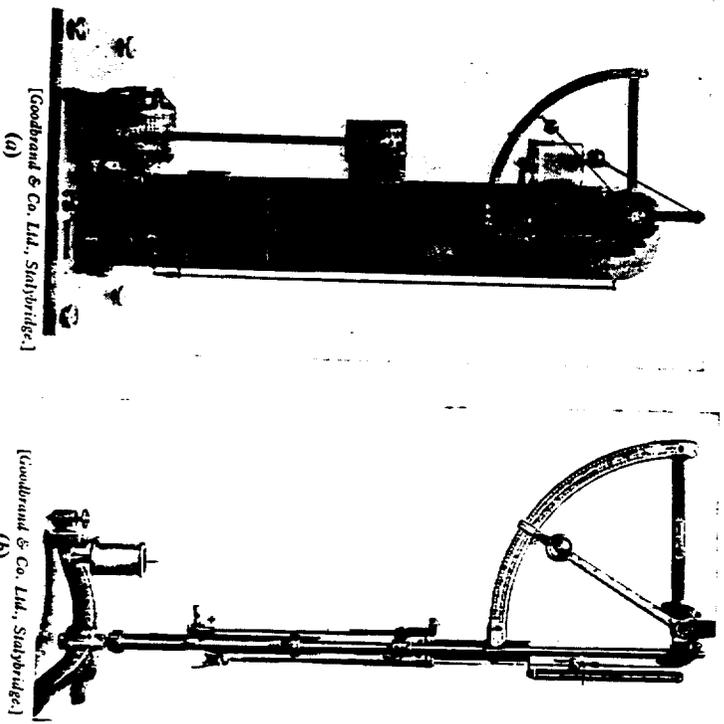


FIG. 5.—Single Thread Tester (constant rate of extension). This machine simultaneously measures breaking load and elongation at break: (a) This up-to-date model is driven by an electric motor. (b) An earlier model, which depended not on a motor but on the gravitational fall of a plunger into an oil bath, was used for decades and played a significant part in the development of new fibres.

Elasticity

The elasticity of a fibre is its ability to recover from strain. If a fibre is stretched 10 per cent—*i.e.*, 100 cm. becomes 110 cm., and then, on release of the tension, it reverts to its original length of 100 cm.—it is perfectly (or 100 per cent) elastic. If, on the other hand, it contracts to 102 cm., then it is 80 per cent elastic; if it contracts to 104 cm., it is 60 per cent elastic. Usually fibres have a high elasticity for low stretches—*i.e.*, if stretched 5 per cent they regain very nearly their original length, but they may have only a relatively low elasticity for high stretches. A fibre with a low elongation at break may have a high elasticity, and, conversely, a very extensible fibre may have only a low elasticity. It is important to distinguish clearly between "elongation at break" and "elasticity".

Breaking Length

Occasionally the strength of a fibre will be expressed as "breaking length". This is the length of a fibre which will just break under its own weight, and it is usually very long. If we consider a viscose filament with a tenacity of 2 grams per denier, we imply that a length of 18,000 metres will just break under its own weight—*i.e.*, the breaking length is 18 km. Similarly a yarn with a tenacity of 4 grams per denier will have a breaking length of 36 km. The strongest yarns hitherto made on a manufacturing scale have breaking lengths of about 80 km. It will be appreciated that the breaking length of a 100-denier yarn will be the same as that of a 2-denier single filament, because, although the former is stronger, it is proportionally heavier.

Stress-Strain Diagrams

The stress-strain diagrams of fibres and yarns are often very informative. In them the strain—*i.e.*, the elongation undergone by a fibre or yarn per unit length—is plotted against the stress, or load applied to it.

The stress-strain diagram—or "characteristic curve", as it is also called—is obtained by using a strength-testing machine of autographic type. The testing machine shown in Fig. 5(a) is supplied as an autographic model; the axes of the diagram it records are at an angle of 45°. Other machines, including the Inclined Plane Tester, shown in Fig. 8, give diagrams in which the axes are at 90°. The latter machine operates at a constant rate of loading, the former at a constant rate of extension. For everyday use in the laboratory and for plant control the writer's preference is for the machine

shown in Fig. 5, but for prototype testing of fibre and yarn characteristics the Inclined Plane model is preferred.

Instron Testers. These are the most widely used in the industry today. Compared with the old plunger-in-oil type they are heavy and expensive. Like them, they are constant rate of extension machines. The fibre sample is gripped by the two jaws shown in Fig. 6 and an electric motor started; the upper jaw moves upward at a rate of 20 mm. per minute and the recording chart moves horizontally at 100 mm. per minute. The machine's output is a stress-strain curve of the type shown in Fig. 7. Other speeds can be used, and the load range 0-10 kg. in the curve shown in Fig. 7 can be changed. The basic function of the instrument is to plot load against extension (stress-strain) curves for all types of textile materials. Other properties, viz. stress relaxation, cyclic loading effects or hysteresis and resilience, can also be evaluated. There is an excellent booklet "Mechanical Testing of Polymeric Fibrous Materials" written by G. A. M. Butterworth and N. J. Abbott and published by Instron Ltd. at High Wycombe. Those who want to know a little more than most about textile testing should get it.

If the stress-strain curve is a straight line, then the fibre is obeying Hooke's Law, and so long as the "curve" is straight, the fibre will be elastic. Usually, after a very few per cent extension the elongation of the fibre becomes greater than would be required by the straight-line curve. This generally means that plastic flow is setting in, and that the fibre is no longer truly elastic. The *yield point* corresponds to the break in the curve where it departs from the straight line. For most fibres this break takes place very early.

A fibre which will be most satisfactory for textile purposes is one that does not stretch much for small loads, so that during winding it does not stretch appreciably; the advantage of this is that even if the winding tension varies slightly from spindle to spindle, the yarn will not suffer seriously different degrees of stretch from spindle to spindle, as it would if it were susceptible to high stretches for very small loads. Consequently a stress-strain diagram which for small loads up to, say, 0.2 or 0.3 gram per denier is straight, is desirable. A fibre which gave the stress-strain diagram shown in Fig. 9 would, other things being equal, be preferred to another fibre which gave that shown in Fig. 10 in so far as freedom from liability to winding strain was concerned. But it is impossible to have every desirable characteristic in any one kind of fibre, and there are other good reasons for preferring fibres with the Fig. 10 type of characteristic curve to those with the Fig. 9 type. It is usually found that the

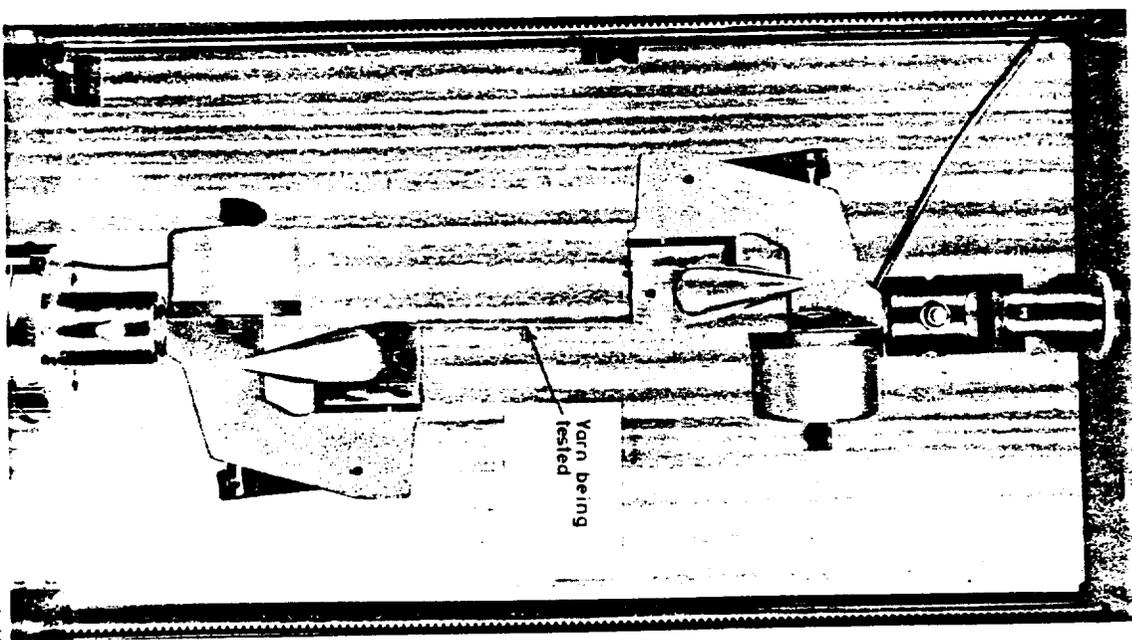


FIG. 6.—A sample of cord mounted in a pair of grips, designed to avoid fracture. The sample is clamped between two flat blocks and is then bent round a radius. Fracture of a sample between flat grips sometimes happens and is a nuisance in the testing room. These special grips avoid this trouble.

[Instron Ltd.]

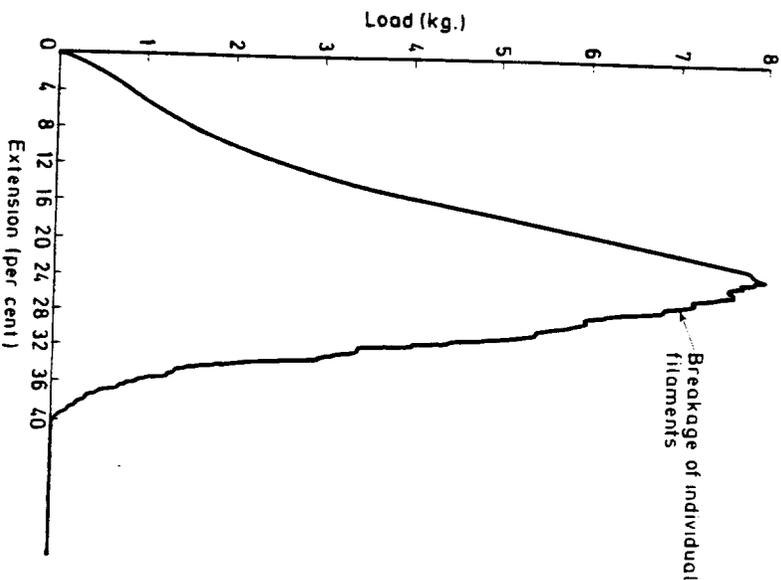


Fig. 7.—Stress-strain curve made by an Instron 1026 of a nylon cord, probably of about 1,500 denier, test length 5 cm., which begins to break after an extension of 1.2 cm. or 24 per cent. Breaking load is about 8 kg., time to begin to break about 29/100 min., say 17½ sec.

Fig. 10 type have a better and softer handle and that they drape better. Most fibre curves have inflexions as in Fig. 10 but in some it is much more marked than in others; cellulose acetate (Fig. 97) has a more pronounced inflexion than viscose rayon (Fig. 76) and is softer to the touch. Wool and the regenerated protein fibres have the best handle of all and they all have a low initial modulus (*cf.* p. 321) and a high compliance ratio (*cf.* p. 322) which appears on the characteristic curve (Fig. 193) as a flattening for moderate extensions. It is probably true to say that the fibres with the softest handle are

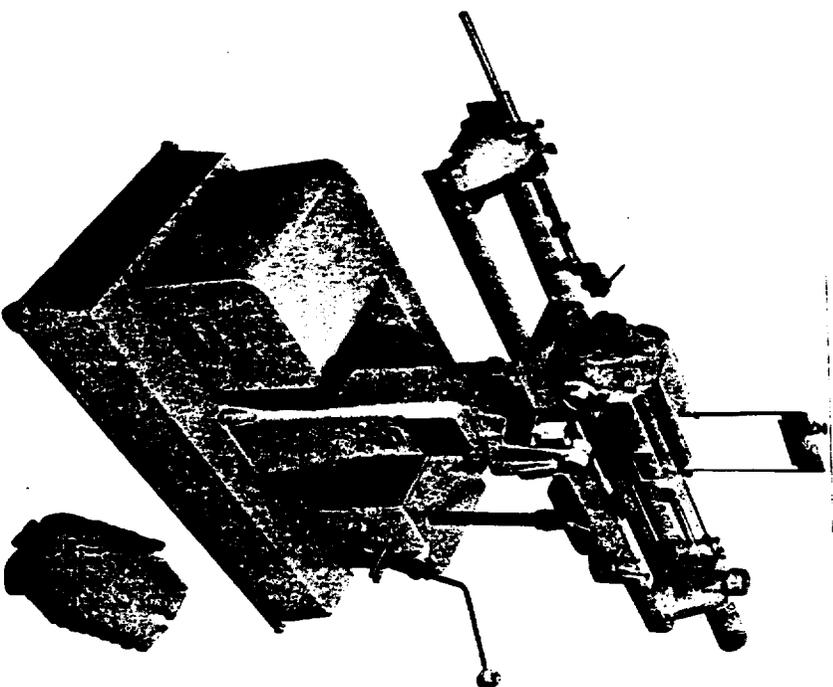


Fig. 8.—Inclined Plane Tester (constant rate of loading). This machine records the stress-strain diagram for a yarn.

[Scott Testers, Inc.]

those that are most easy to damage by excessive winding tensions. The fibre that is the best for soft and comfortable underwear is unlikely to be the best for industrial uses such as ropes and belts where high strength and good recovery are essential.

The following fibres have their stress-strain diagrams recorded in this book; viscose rayon (Figs. 76, 103), cellulose acetate rayon (Fig. 97), Zantrel (Fig. 112), nylon 6 (Fig. 148), nylon and Terylene (Fig. 154), Kodel (Fig. 169), Dynel (Fig. 175), Orlon (Figs. 186, 187, 193), Acrilan (Fig. 198), and Darvan (Fig. 203). They should be compared.

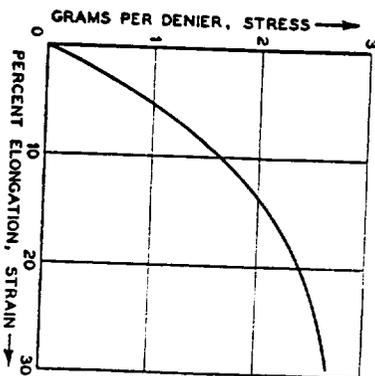


Fig. 9.—Stress-strain diagram of fibre with desirable winding characteristics.

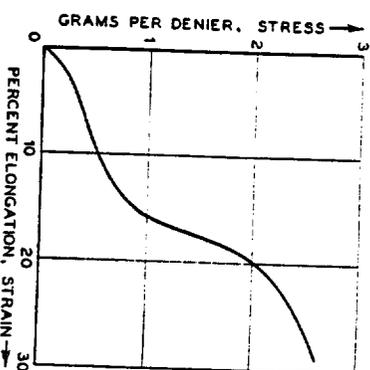


Fig. 10.—Stress-strain diagram of fibre which might easily be strained during winding.

Regain

All fibres exposed to the atmosphere pick up some moisture. The quantity of moisture picked up varies with the relative humidity and with the temperature of the atmosphere. Measurements are therefore made at standard conditions, which are arbitrarily fixed at 65 per cent relative humidity (R.H.) and 70° F. It takes some time—often a matter of hours—for a bundle of fibres to become in equilibrium with an atmosphere; if fibres are to be tested they should first be “conditioned” for several hours in a conditioning room maintained at 65 per cent R.H. and 70° F. If the fibres are in the form of a thick, highly twisted yarn or a heavy fabric they may require two days to reach equilibrium; for small bundles of loose fibres two hours is usually sufficient. Usually the moisture content of a fibre or yarn is described as regain.

Definition. The regain of a fibre (or yarn) is the percentage weight of moisture present, calculated on its oven-dry weight. (“oven-dry weight” is the constant weight obtained by drying the fibre at a temperature of 105–110° C.)

Thus, if 100 parts by weight of a textile material contain 10 parts by weight of moisture, the regain is $100 \times 10/90 = 11.1$ per cent, and the equivalent moisture content is 10 per cent. Note carefully that the regain is always calculated on the oven-dry or bone-dry weight of the fibre or yarn. It follows that the percentage regain is always greater than the percentage moisture content.

Some fibres absorb moisture much more readily than others; those that pick up more moisture than others are said to be more

hygroscopic, and under similar conditions have higher regains. The molecular structure of a fibre largely determines its hygroscopicity. Cellulose fibres such as viscose rayon, which are characterised by the possession of a large number of hydroxyl groups, have high regains; polyvinyl fibres, which have no strongly polar groups, have very little affinity for water and have low regains.

Regain varies greatly with atmospheric conditions, and indeed the determination of the weight of wool under standard atmospheric conditions has always been a matter of commercial importance and of need for care; a consignment of wool charged for as 100 lb. may appear to weigh only 96 lb. when received, and care has to be taken to ascertain the weight of a sample under standard conditions (often simplest to weigh bone dry and calculate what the weight with the agreed regain would be). Nylon has a low regain compared with the natural fibres but a high one amongst the group of synthetics. Variation of nylon's moisture regain with relative humidity of the atmosphere at 25° C. is as shown in the following table; the measurements were made on undrawn nylon.

R.H. of atmosphere (“%”)	Moisture regain of undrawn nylon.
25	1.7
40	2.9
55	3.7
70	5.2
85	7.4
90	8.3

It has sometimes been observed, for example with acrylic fibres (p. 579), that the moisture regain is higher when equilibrium is approached from the wet end, *i.e.*, by drying a wet fibre, than when approached from the dry end, *i.e.*, by wetting a dry fibre. This affords an example of hysteresis. A typical example, for a cheap muslin fabric, is shown in Fig. 11. At a relative humidity, for example, of 50 per cent, the moisture content of the fabric is greater when it is approached from the wet state than from the dry state.

Determination of Moisture Content

Until recently the usual method for determining the moisture content of a fibre has been to dry it and observe the decrease in weight on drying; nowadays electrical and other devices are available which enable very rapid determinations to be made of moisture content.

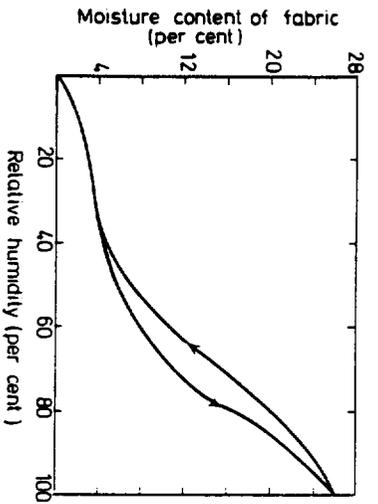


FIG. 11.—The moisture content of a fabric at a given R.H. is different as it is approached from the dry or the wet side. The hysteresis curve illustrates this.

(Textile Manufacturer)

Thermogram Method. This gives accurate results but the apparatus is costly and requires expert supervision. Small samples of fibre or fabric are dried at constant temperature and their weight measured at time intervals. The drying curve (weight-time) is automatically recorded.

Drying to Constant Weight. All that is necessary is an oven in which fibre can be kept at about 105° C.; the fibre is removed at intervals and weighed. When two or three successive weighings are the same, it is judged that dryness has been reached. The only difficulty about this method is that the sample has to be removed from the oven to be weighed; in fact it is usually popped into a glass weighing-bottle with a ground glass cover so that there is not much opportunity for it to pick up moisture. This method is the simplest of all, and in the author's view is very good. Anybody can carry it out faithfully with a little practice, and weighing is a measurement that can be made exactly and easily. For mills which do not possess laboratories this is probably the best method.

Conditioning Room. This method avoids the difficulty of exposing the sample to moist air while it is being weighed; its disadvantage is that it is slow and that it requires a conditioned room kept at constant temperature and humidity. In large plants, such rooms are available and staff work in them making physical measurements, e.g., of breaking load and extension of fibres. Given a certain set of conditions, say 65 per cent relative humidity and 70° F. (21° C.), the fibre

will eventually reach an equilibrium state. It can be weighed when taken into the room and repeatedly weighed until it reaches a constant weight; if for example it is cellulose acetate, the equilibrium state will be reached with a moisture content of 6 per cent. The advanced worker will prefer this method to that of hot drying; it does no permanent damage to the fibre, whereas hot drying may alter its structure. Whatever method is used, practice is necessary, including practice with samples of fibre of known moisture content.

Sugar Solution Method. This is novel and interesting and has been described by A. F. Miaglyachenko, L. M. Patsova and N. V. Poflavets [*Legkaya Promyshlennost* (Light Industry), 1970 (4), 13-16]. A 5 per cent sugar solution is flooded over a sample of fabric which has been dried at 105° C., and the fabric is soaked in it for 8 hours to allow equilibrium conditions to obtain. The sugar solution is then filtered off and its concentration is easily and quickly determined by measuring its refractive index in an Abbe refractometer, a measurement which young assistants can easily carry out. The fabric will have adsorbed water, but no sugar, so that the concentration of the sugar solution will have increased, and this increase will indicate how much water the fabric has picked up. In an example, the dry weight of the fabric was 5.0294 grams; the weight of the 5.000 per cent sugar solution was 25.2550 grams containing 1.26275 grams sugar. At the end of the experiment the solution contained 5.060 per cent sugar, so that the weight of this solution must have been 1.26275 divided by 0.05060 or 24.9555 grams, which is 0.2995 grams less than the starting solution. Accordingly, a piece of fabric weighing 5.0294 grams has picked up or adsorbed 0.2995 grams water, i.e., 5.94 per cent. The method measures the equilibrium value of adsorbed moisture content; this should be fairly constant for fibres of one kind such as viscose, but will be very different from one kind of fibre to another, e.g., viscose and cellulose acetate.

Soviet Numbering System

The numbering system used by the Russian industrialists is a metric one; it indicates the length in metres of a yarn or filament that weighs one gram. The equivalent deniers (grams per 9,000 metres) and tex (grams per 1,000 metres) and millitex (milligrams per 1,000 metres) values for some metric numbers are shown in the following table:

Soviet metric number	Denier	Tex	Millitex
1	9,000	1,000	1,000,000
10	900	100	100,000
50	180	20	20,000
100	90	10	10,000
500	18	2	2,000
1,000	9	1	1,000
1,500	6	0.67	667
3,000	3	0.33	333
4,500	2	0.22	222
9,000	1	0.11	111

A convenient method of conversion is:

Russian metric number = $\frac{9,000}{\text{denier}}$ The higher the Russian metric

number, the finer is the yarn or filament and in this respect it is in line with our own cotton and worsted numbering systems.

FURTHER READING

N. Eyre, "Testing of Yarns and Fabrics", pp. 27-48. Textile Manufacturer Monograph No. 4 (1947) (denier, tenacity, twist, etc.).
M. V. Forward and S. T. Smith, "Moisture regain of 66 nylon continuous filament yarn", *J. Text. Inst.*, 46, T158-T160 (1955).

THE STRUCTURE OF FIBRES

CHAPTER 2

WHAT is the one feature common to all fibres? Let the whole gamut of them pass through the mind: cotton, flax, hemp, jute, ramie, silk, tussah, wool, rabbit, alpaca, mohair, llama, camel, viscose, cellulose acetate, nylon, Vinyon, Velon, Pe Ce, Ardi, Vicara, alginate, glass, asbestos, stainless steel, aluminium, and all the others. Most are organic, a few, like glass and asbestos, are inorganic; some are of animal origin, some of vegetable; some have continuous filaments, others have short filaments; some are transparent, others are opaque; some will burn, others will not; some are weak, others are strong. With almost any property but one the diversity of fibres will readily provide examples in which the property is well-marked—or in which it is to all intents and purposes absent.

THE SHAPE OF FIBRES

One property, however, is common to all fibres—that is, that all are very long in relation to their breadth. A little reflection will show that a high length: breadth ratio is the essential characteristic of a fibre. The material of which the fibre is constituted does not determine that it will be a fibre; there are many substances—of which mention can be made of nylon and of cellulose acetate—that are used in the form of moulded plastics as well as in fibre form. It is purely and simply the *shape* that is characteristic of a fibre. One would not think of a nylon moulding or of a cellulose acetate sheet as a fibre. The primary characteristic—the one indispensable prerequisite for a fibre—is a high length: diameter ratio.

Length: Breadth Ratios of Natural Fibres

The universal possession by fibres of the high length: diameter ratio may be observed by examination of the following typical figures for some of the natural fibres:

Fibre.	Typical length.	Typical diameter.	Length: diameter.
Cotton	1 in.	0.0007 in.	1,400
Wool	3 in.	0.001 in.	3,000
Flax (ulmimate)	1 in.	0.0008 in.	1,200

CHAPTER 9
VISCOSE RAYON

The process of making viscose yarn was discovered by C. F. Cross and E. J. Bevan—two chemists who brought about a much better understanding of the chemistry of cellulose. The process was discovered in 1891, and patented by Cross, Bevan and Beadle in 1892, but took some considerable time to establish itself.

Development of Viscose

The greatest single factor in the development of the viscose process has undoubtedly been the support given to it by Courtaulds, Ltd., although there have naturally appeared other viscose producers. The pioneer work was undoubtedly carried out by Courtaulds, Ltd., who not only founded and developed an important new industry, but also introduced it to America under the name "The American Viscose Co." During the 1939-45 War this American Company was sold to American interests in order to provide dollars for Britain. Other names prominent in viscose manufacture are du Pont de Nemours & Co. (but see p. 163), the Industrial Rayon Corporation and the American Enka Co. in America; Sna Viscosa in Italy; the Glanzstoff Corporation in Germany and Toyo in Japan.

In this country Coventry was the home of the first viscose spinning-plant, and immense quantities of yarn still come from there. The present happy position of the viscose industry not only in this country, but throughout the world, is undoubtedly largely due to the industrial genius of the late Mr. Samuel Courtauld.

In 1912 it was unusual to see artificial silk in a Lancashire mill. I remember, as a boy at about that period, seeing a few bobbins of it, and being considerably impressed; it was still so unusual as to be a novelty. Nor was it very good, for when washed the fabrics into which it was made nearly fell to pieces on account of its very low wet strength. However, even at that time it found employment as effect threads in stripes for dress materials and shirtings. In later years the wet tenacity was greatly improved.

Contrast that state of affairs with a world production of nearly 3 million tons of viscose rayon in 1964. The growth in production may be realised from the following figures:

Year	World production of viscose rayon.
1900	1,000 tons
1910	5,000 "
1920	15,000 "
1930	200,000 "
1940	1,100,000 "
1950	1,300,000 "
1960	2,300,000 "
1963	2,700,000 "
1967	2,700,000 "

Such a consumption will eventually make inroads on the timber supplies. However, cellulose is abundant in the vegetable kingdom and there are many other possible sources of it than timber. Wheat straw, esparto grass and bamboo all contain about 50 per cent cellulose. Bamboo is being developed in India as a cellulose source. Timber does however have the big advantage as a raw material for fibres that it is abundant in the arctic and sub-arctic forest regions, so that its growth does not interfere with the world's food supply.

One factor that has had a considerable bearing on the growth of the consumption of viscose rayon is the success which has attended the introduction of viscose staple fibre. This material which, at first, had a rough and unattractive appearance and handle and was easily crushed and creased, has been vastly improved, and is now an attractive and deservedly popular material.

Viscose rayon has always been the cheapest of the artificial silks, and probably for that reason, more than any other, its production is much greater than that of all other artificial fibres taken together.

It is surprising to find nowadays that some of the older spinners of viscose rayon, presumably dazzled by the benefits of the synthetic fibres, are giving up viscose spinning. Du Pont, one of the biggest, have discontinued viscose rayon. Teijin, in Japan, has closed its rayon staple plant at Iwakuni, which had an output of 58 million lb. of yarn per annum. This plant had been built before the war, and it latterly required so much maintenance that it had become uneconomic to operate. We shall possibly see in the next decade much of the cellulosic fibre manufacture drift to India and China. Japan, too, will probably reduce her production, and spend more and more of her skill and industry on the synthetic fibres.

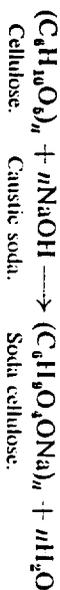
The increase in the production of rayon, its distribution between continuous filament and staple, and the relation it bears to the production of natural fibres, are discussed in Chapter 51.

Chemical Nature

Viscose rayon is regenerated cellulose. The cellulose comes from wood, of which it is the major constituent. It is purified, treated with caustic soda, which converts it into alkali cellulose, then treated with carbon disulphide, which converts it into sodium cellulose xanthate, and then dissolved in a dilute solution of caustic soda. This solution is then "ripened", the solution becoming at first less viscous and then increasing nearly to its original viscosity; it is then spun into an acid coagulating bath, which precipitates the cellulose in the form of a viscose filament. The cellulose which constitutes the final filament differs chemically from the original cellulose of the wood in only one respect—that it has suffered some degradation during the manufacturing processes: the very long cellulose molecules have been partly hydrolysed and have been broken down into shorter, although still very long, molecules. When artificial fibres are made by chemical processes from naturally occurring polymers, as in the case of viscose from wood cellulose, or Bemberg or cellulose acetate from cotton cellulose, or alginate from seaweed, it is desirable so far as possible to keep the inevitable degradation of the materials to a minimum. If the natural long-chain polymers are broken down considerably there is a significant loss in strength and fibrous properties. In the present state of our knowledge some breakdown is inevitable, but ways have been found of reducing this depolymerisation very considerably, compared with that which obtained in the earlier days of the industry. It should never be forgotten that good fibres can be made only from long polymeric molecules and that, as a result, both in the manufacture of the fibre and in processes to which the yarns and fabric made from it are subjected, conditions which encourage hydrolysis should not normally be allowed to obtain. In viscose, the cellulose molecules are about one-quarter as long as those in the wood cellulose from which it was made.

Chemical Reactions for Manufacture. The chemical reactions that are involved in the manufacture of viscose are as follows:

1. The cellulose is treated with a 17.5 per cent solution of caustic soda which converts it into soda cellulose. The reaction is usually expressed:



Cellulose:

Caustic soda:

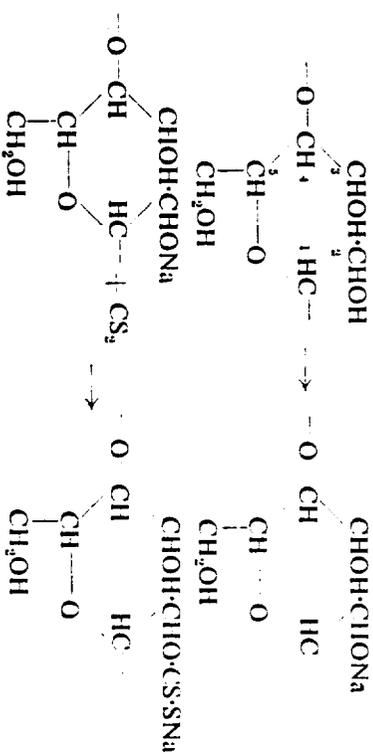
Soda cellulose:

and, according to this equation, 162 parts by weight of cellulose should require 40 parts of caustic soda. In practice it is found that twice as much caustic soda as this is required.

The reaction between the soda cellulose and the carbon disulphide may be represented:



Each glucose residue in the cellulose polymer chain must be thought of as reacting in the following way.



The reaction takes place on the hydroxyl group in position 2 in the glucose residues in the cellulose polymer. According to the above equation 162 parts by weight of cellulose should require 76 parts of carbon disulphide. In practice it is found that only about 70 per cent of the theoretical quantity, *i.e.*, 52 parts of carbon disulphide, is required. The measurement of the requisite quantity of carbon disulphide is shown in Fig. 52.

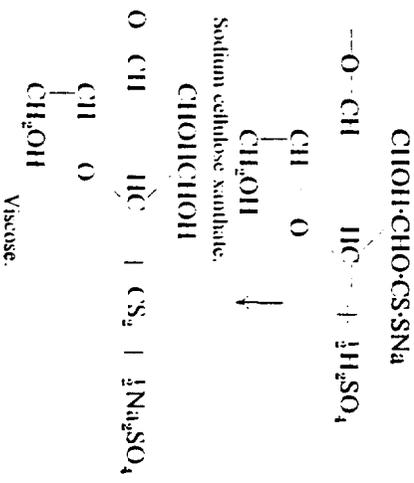
When the sodium cellulose xanthate is dissolved in weak caustic soda to form the viscous solution known as "viscose" the xanthate radicals probably combine loosely with the molecules of caustic soda.

When the viscose solution is first made, it is very thick. On standing, it becomes thinner and then, later, more viscous again. This process is known as "ripening", and whilst it is going on, some of the sodium cellulose xanthate decomposes, regenerating cellulose which is maintained in emulsion form by that part of the sodium cellulose xanthate which is still undecomposed, this latter part acting as a protective colloid. If the ripening process was allowed to proceed far enough, the cellulose would eventually be precipitated when there was no longer a sufficient amount of the undecomposed sodium cellulose xanthate to hold it in emulsion; but in practice, just before this precipitation is due to begin, the solution is spun. It



FIG. 52.—The requisite quantity of carbon disulphide being measured for addition to a batch of "crumbs".

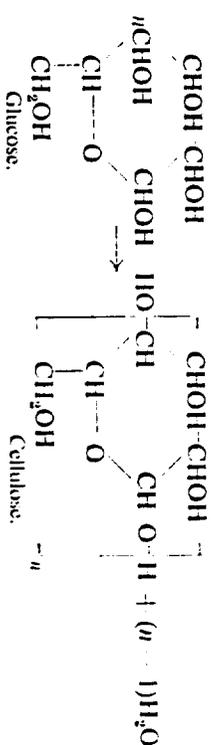
is spun into a coagulating bath of sulphuric acid which completes the conversion of the sodium cellulose xanthate to cellulose:



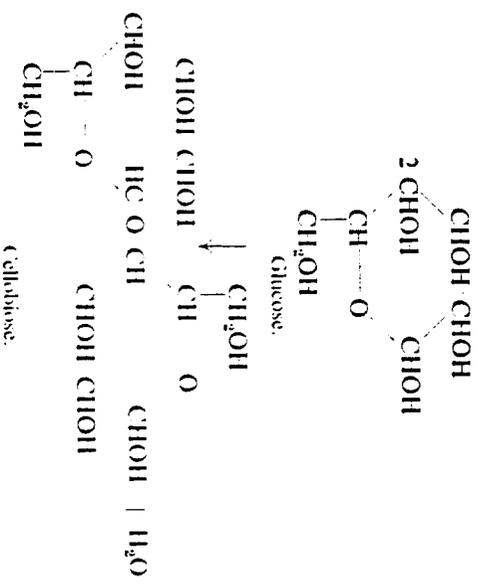
This completes the series of chemical reactions by which viscose is made. Essentially they consist of the following stages:

1. Wood cellulose and concentrated caustic soda react to form soda cellulose.
2. The soda cellulose reacts with carbon disulphide to form sodium cellulose xanthate.
3. The sodium cellulose xanthate is dissolved in dilute caustic soda to give a viscose solution.
4. The solution is ripened.
5. It is extruded into sulphuric acid which regenerates the cellulose, now in the form of long filaments (viscose rayon).

It will be appreciated that natural cellulose is built up of glucose residues in this way:



The first step in this natural polymerisation is the formation of one molecule of cellobiose from two molecules of glucose



When the polymerisation proceeds further the molecules of cellobiose condense and form a long string of glucose residues. In wood

cellulose the molecule contains about 1,000 of these glucose residues. In viscose rayon the cellulose contains about 270. The cellulose molecules have been broken down in the chemical processes by which the viscose is made, but apart from the fact that the viscose cellulose molecules are shorter than the wood cellulose molecules, they are similar. With that one exception, viscose yarn is the same chemically as wood cellulose. There is also a difference in the *packing* of the molecules between native and regenerated celluloses.

MANUFACTURE

Preparation of the Wood Pulp. The starting material is timber, usually spruce. After it has been felled it is floated on rivers to the mills. Here the bark is removed and the wood is chipped into pieces about $\frac{3}{4} \times \frac{1}{2} \times \frac{1}{4}$ in. The chips are treated with calcium bisulphite, and the treated chips then cooked with steam under pressure for fourteen hours. This treatment does not greatly affect the cellulose, but it decomposes and solubilises the encrusting substances, so purifying the cellulose. After cooking, the mass is diluted with water on which the pulp floats; the pulp is then sucked through slots about 0.2 mm. wide. It is concentrated to 30 per cent cellulose content, bleached with hypochlorite and converted into paper board. The bleaching that the cellulose receives in these preparatory stages greatly reduces the need for bleaching of the rayon, and in fact some rayon is not bleached—*i.e.*, the only bleaching it has undergone is the pulp bleach.

Steeping and Pressing (Formation of Soda Cellulose). The flat, white sheets of board contain about 90-94 per cent of pure cellulose. They are first conditioned by storing in a room at a definite humidity and temperature. This conditioning is necessary so that a known weight of cellulose can be weighed out for each batch (Fig. 53). The sheets are then stacked vertically in the press (Fig. 54), and then soaked in a 17.5 per cent solution of caustic soda for from one to four hours. This process is known as *steeping* or *mercerising*. The boards become greatly swollen, and the hemicelluloses are dissolved in the caustic soda, and turn the liquor brown. About 8.2 per cent of the original wood pulp dissolves. The cellulose itself is swollen, but not dissolved.

Then the excess alkali is pressed out by a hydraulic ram in the press—the unit in which the soaking has been carried out. The pressing leaves a moist mass of soda-cellulose, which passes straight into a shredding machine.

Recovery of Caustic Alkali. The alkaline liquors that are ex-



FIG. 53.—The sheets of wood pulp are carefully weighed for each batch.



FIG. 54.—The wood pulp is placed in the press prior to running in the caustic soda.

pressed are allowed to diffuse through parchment-paper membranes. The caustic soda passes through the membrane, and, after being made up to strength by the addition of fresh alkali, is re-used. Ultimately, when it is so foul that it can no longer be used, it is disposed of to soap-works. The recovery of alkali is an important factor in the economic operation of the viscose process.

Shredding. The shredding machine consists of a drum inside which revolve a pair of blades with serrated edges. The shredders are water-cooled, and will take 200 lb. of pressed soda-cellulose at a time. In two to three hours they break it up into fine "crumbs".

Ageing. After shredding, the "crumbs" are aged. They are contained in a galvanised vessel with a lid, and through oxidation with atmospheric oxygen, degradative changes set in. Some depolymerisation occurs, and the degree of polymerisation (number of glucose residues in a cellulose molecule) falls from about 800 to 350 in this process. Of recent years it has been found possible, by using a rather higher temperature, which is automatically controlled, to complete the ageing in from one to one and a half days. (If it were allowed to continue for a matter of months the crumbs would become water-soluble when the degree of polymerisation fell below 100.) Until recent years it was customary to age for about three and a half days at 22° C.—*i.e.*, in a comfortably warm room. The higher the temperature, the more rapidly does ageing—which is mainly a process of depolymerisation—proceed.

The American firm, Oscar Kohorn & Co., Ltd., who are primarily machinery designers and manufacturers, have developed a "Rapid Ageing Process", in which the ageing of the soda-cellulose is carried out during the shredding process, by careful control of temperature and other physical conditions. This saves a process in practice, together with labour costs, and cuts down the time necessary to make viscose. It is claimed that in the Kohorn process the quality and filterability of the final viscose are better than usual because of the reduced oxidation and degradation that take place during ageing.

Ageing consists essentially of storage under controlled atmospheric conditions. Oxidation and depolymerisation occur, and these changes considerably influence the properties of the viscose yarn that will eventually be made.

Churning (Xanthation or Sulphitising). After ageing, the soda-cellulose crumbs are introduced into rotating air-tight hexagonal churns (Fig. 55). About 10 per cent of their own (crumbs) weight of carbon disulphide is added (Fig. 52), and the crumbs and disulphide are churned up together; a deep orange, gelatinous mass of sodium cellulose xanthate is formed. Note that theoretically 162

parts of cellulose require 78 parts carbon disulphide. The crumbs contain about 30 per cent cellulose, so that 162 parts crumbs should need 23 parts carbon disulphide—*i.e.*, 100 parts should need 14 parts carbon disulphide, so that the quantity actually used, 10 parts, is about 70 per cent of the theoretical quantity.

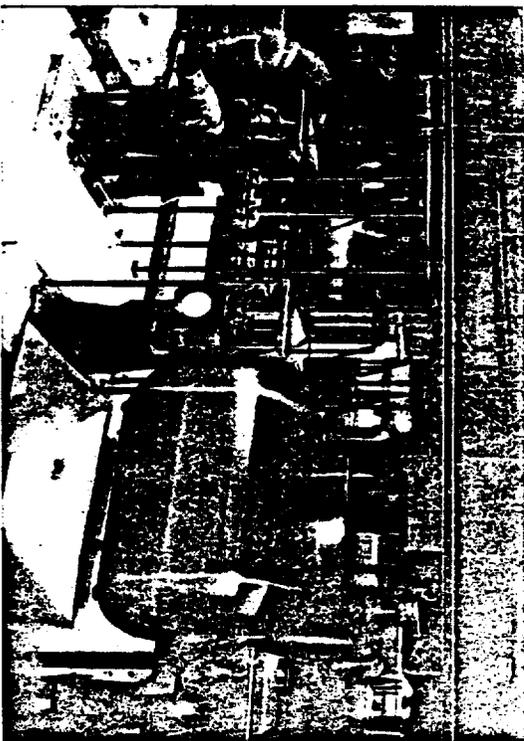


Fig. 55.—Xanthating burater in a plant installed by Oscar Kohorn & Co., Ltd., New York.

The "crumbs" are churned with a definite quantity of carbon disulphide.

Churning is continued for about three hours, the churns rotating at about 2 r.p.m. Each churn (which is water-jacketed) holds a charge of about 200 lb. At the completion of churning the vessels are exhausted by vacuum to remove ill-smelling vapours and the charge is dumped in mixers. (Sometimes churning and mixing may be carried out in the same, specially designed, vessel.)

Mixing (Solution). In the mixers the sodium cellulose xanthate is stirred with dilute caustic soda solution for four to five hours, the vessel being cooled. The xanthate dissolves to a clear-brown, viscous liquid, similar in appearance to honey. This liquid is known as "viscose", but is still too impure, too aerated and too young to spin. It contains about 6.5 per cent alkali and 7.5 per cent cellulose. It is transferred to a secondary mixer or blender, which takes the charges from eight primary mixers. Note that it is always desirable

to blend the materials from which rayon will eventually be made, as inequalities are thus balanced out and there is a better chance that the rayon will be uniform in quality and characteristics.

In the secondary mixer or blender the viscose is stirred and pumped round. As it still contains some undissolved fibres from the original wood pulp, fibres which have resisted all the chemical treatments, it is filtered. The first filtration is carried out through cotton-wool, and the viscose is then twice filtered through cotton filter-cloth. If a delustrated yarn is eventually required, a pigment, perhaps 2 per cent on the weight of the cellulose of titanium dioxide, will be added to this solution and dispersed by stirring. Air-bubbles are then removed by exposing the viscose in air-tight tanks to a vacuum.

Ripening. The viscose solution is stored for 4 to 5 days at 10–18°C., and during storage it ripens. During the ripening the viscosity at first falls, and then rises, so that by the time the solution is ready to spin, the viscosity has risen almost to its original value. Ripening is an essential part of the viscose process; "young" viscose cannot be spun satisfactorily; neither can viscose that is even a few hours too old. Two tests which are available to determine when viscose is ripe enough to be spun are as follows:

1. *Acetic Acid Test.* Before it is ripe the viscose solution will dissolve in 40 per cent acetic acid, but when it is ripe the viscose will precipitate in this acid.

2. *The Hottelroth (Ammonium Chloride) Test.* Twenty grams of the viscose to be tested are mixed with 30 c.c. distilled water, and to this solution is then added from a burette with stirring, a solution of 10 per cent (wt/wt) ammonium chloride. The ripeness figure is the number of c.c.s of ammonium chloride solution necessary to bring about coagulation of the viscose to a gelatinous condition. The lower the number, the riper the viscose.

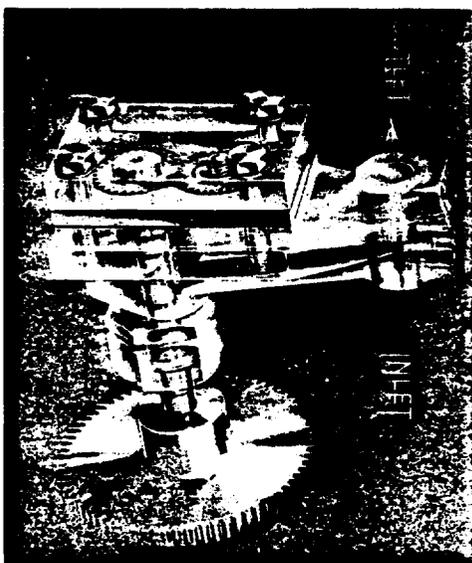
Of these two tests the acetic acid test is no longer used; the Hottelroth, called after its originator, is most universally employed.

When the viscose solution is ripe, it is drawn off to settling tanks, where all air-bubbles are removed from it by exposure to a vacuum for twenty-four hours. This is essential, for any bubbles in the spinning solution would arrest the spinning and there would be discontinuities in the filaments.

The normal time interval that elapses between the start of the steeping operation and the viscose solution being ready for spinning is about a week, most of the time being taken up in ageing of the alkali-cellulose and ripening of the viscose solution. Probably, in most modern plants, improvements have been effected to reduce this

time to about five days. The Kohorn Process, in which the ageing is carried out simultaneously with the shredding, and in which the normal ripening time has apparently been reduced, cuts down the total time considerably, so that viscose ready for spinning is produced in approximately forty hours from the start of the steeping operation.

Spinning. When the viscose solution is ripe, it is forced by compressed air (2.6–5 atmospheres) to the spinning frames, and there distributed. It is metered by a small viscose pump for each spinning-



[Dobson & Barton, Ltd.]

FIG. 56.—Spinning pump of gear wheel type.

This pump meters as well as pumps viscose solution to the filter canule and thence to the jet. Its metering action ensures uniformity of denier.

head. The viscose pump is usually of the gear wheel type, and the wheels and plates are constructed of stainless steel to resist the etching effect of the viscose with which they come in contact. Pumps used in the early days of rayon spinning did not approach the performance of to-day's gear pump. The pump used on Courtauld's original spinning machine at Coventry in 1903 was a single plunger type. Later came double plunger types, and ultimately the gear pump which has the outstanding advantage that it gives a constant output (so that denier will not vary) irrespective of the input pressure. The viscose, which the pump (Fig. 56) meters continuously, lubricates the pump-wheel shaft. The metering pump's action ensures constant and regular delivery of viscose to the filter and spinning jet, at the exact rate required for the denier being spun. Alteration in the

speed of the pump drive enables the denier to be changed. The pump illustrated delivers 0.6 c.c. per revolution.

From the pump the viscose passes to the filter, which may be either of the candle or disc type, either of which filters the viscose through fabric.

After passage through the filter the viscose passes into the glass "rounder-end", which carries a spinneret (see Fig. 51). The spinnerets are submerged in the acid bath, and are usually arranged so that the filaments emerge almost at right angles to the surface of the bath.

The jet is precision-bored with orifices of diameter usually between 0.05 and 0.1 mm. diameter. The number of holes in the jet, together with the rate of delivery from the spinning pump, and the godet speed (*i.e.*, take-up speed) determine the filament denier. The spinning jet is made from tantalum, or one of the noble metals—*e.g.*, gold, platinum or rhodium—on which the bath liquids have very little action. The drilling of these jets is, as may be imagined, a highly specialised art.

The spinning bath is made of sheet lead. Fresh acid is fed into it by a pipe which runs along its bottom, and a weir overflow controls the level of the bath. A channel carries away overflow from the bath, as well as acid centrifuged from the spinning pot and drips from the godet rollers. The bath contains a solution which consists essentially of 10 per cent sulphuric acid plus sodium sulphate. As the viscose solution passes through the jets into the acid bath, it solidifies into filaments, owing to regeneration of the cellulose. The bath, at a temperature of about 40–55° C., may be made up as follows, although the exact composition will vary from one manufacturer to another:

Sulphuric acid	10 parts by weight
Sodium sulphate	18 "
Glucose	2 "
Zinc sulphate	1 "
Water	69 "

Sometimes, too, magnesium sulphate is a constituent of the bath.

At one time it was usual to use 5 per cent glucose, but for reasons of economy more than 2 per cent is not as a rule used now, and in fact some first-class viscose rayon is spun without any glucose in the bath. The composition of the spinning bath has been arrived at empirically, and it is not safe to describe too boldly the functions of the ingredients, but, with this reservation, they may be indicated as follows: the sodium sulphate precipitates the sodium cellulose xanthate from the viscose solution into the form of filaments, and the sulphuric acid converts it into cellulose; the glucose gives pliability

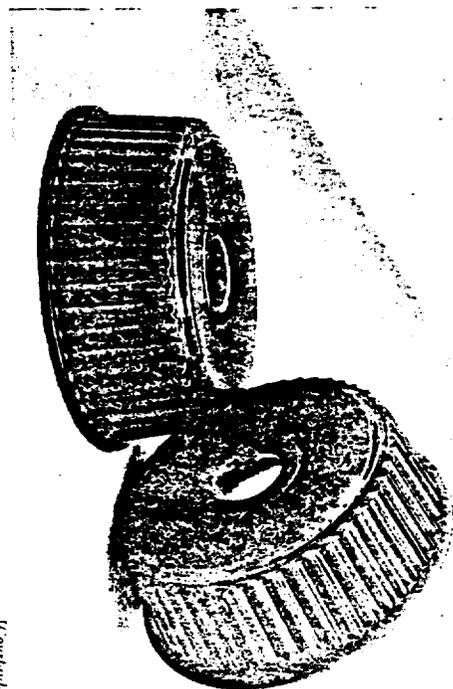
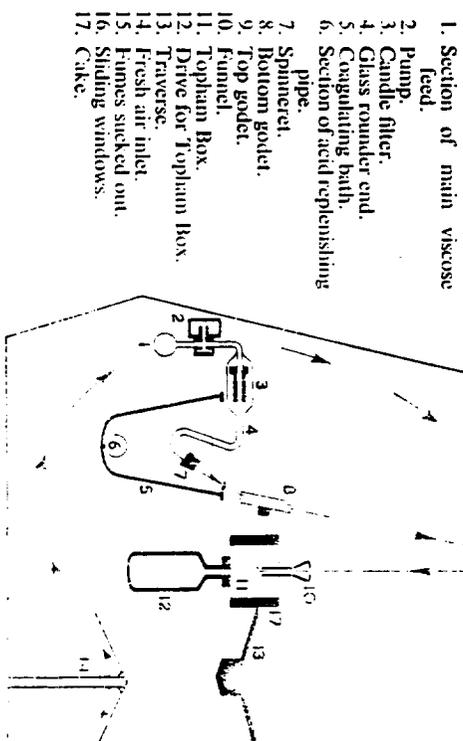


Fig. 57.—Godet rollers.

(continued, p. 175)

These can be seen on the spinning machines in Figs. 60 and 61. Stretch is imparted to the filaments by running the top godet at a higher speed than the bottom godet.

Fig. 58.—Diagram showing viscose rayon spinning essentials. One side of a two-sided machine is shown.



1. Section of main viscose feed.
2. Pump.
3. Glass rounder end.
4. Causticating bath.
5. Section of acid replenishing pipe.
7. Spinneret.
8. Bottom godet.
9. Top godet.
10. Funnel.
11. Topham Box.
12. Drive for Topham Box.
13. Trough.
14. Fresh air inlet.
15. Funnel sucked out.
16. Sliding windows.
17. Cake.

and softness to the yarn, probably because it increases the viscosity of the coagulating bath, and thus retards a little the chemical change from sodium cellulose xanthate to cellulose; the zinc sulphate is responsible for added strength, an important feature, and also for the serrated cross-section, for if it is omitted the filaments are round or oval in section and do not dye so well as when they are serrated or indented. Factors which affect the quality of the viscose rayon are:

1. temperature and composition of the bath;
2. speed of coagulation;
3. length of immersion;
4. speed of spinning;
5. stretch imparted between the godets.

As the filaments emerge from the jet (they do not stick together) they are led to an eye at the surface of the bath, and thence guided round the bottom godet rollers. The godet rollers are illustrated in Fig. 57. The filaments pass from the bottom godet round another guide, made of glass or other acid-resisting material, round the top godet, then over a second glass guide and again round the top godet rollers. The filaments (bunched together as a yarn by the first guide they meet at the bath surface) pass round the godets at the speed of the godets—*i.e.*, they do not slip—and as the top godet is driven faster than the bottom, the filaments are stretched, usually about 100 per cent, between the bottom and top godets. The yarn passes from the top godet downwards through a glass funnel to the centrifugal spinpot, known as the Topham Box or Topham Pot. The diagram in Fig. 58 illustrates the essentials of the viscose spinning process. Fig. 59 shows a complete Viscose Rayon Spinning Machine. Figs. 60 and 61 show Viscose Rayon Spinning Machines in operation.

Spinning Speeds. There has been a gradual increase in the spinning speed as the viscose process has developed. Probably most viscose rayon is spun within the range 60–80 metres per minute. Attempts to modify the process to run at higher speeds have been made; the von Kohorn high speed spinning system for viscose filament yarns incorporates some modifications to the precipitation baths and enables speeds of 140–150 metres per minute to be obtained and it can be used for any denier.

The Topham Box. This is the take-up device for cake-spun viscose rayon. It consists essentially of a bucket on a spindle driven by an electric motor. The complete assembly is shown in Fig. 62. Fig. 63 shows a cut-away view of the bucket of a Topham Box. Fig. 64 shows a cut-away view of another type of Topham Box; in this the cake of viscose rayon can be seen inside the bucket.

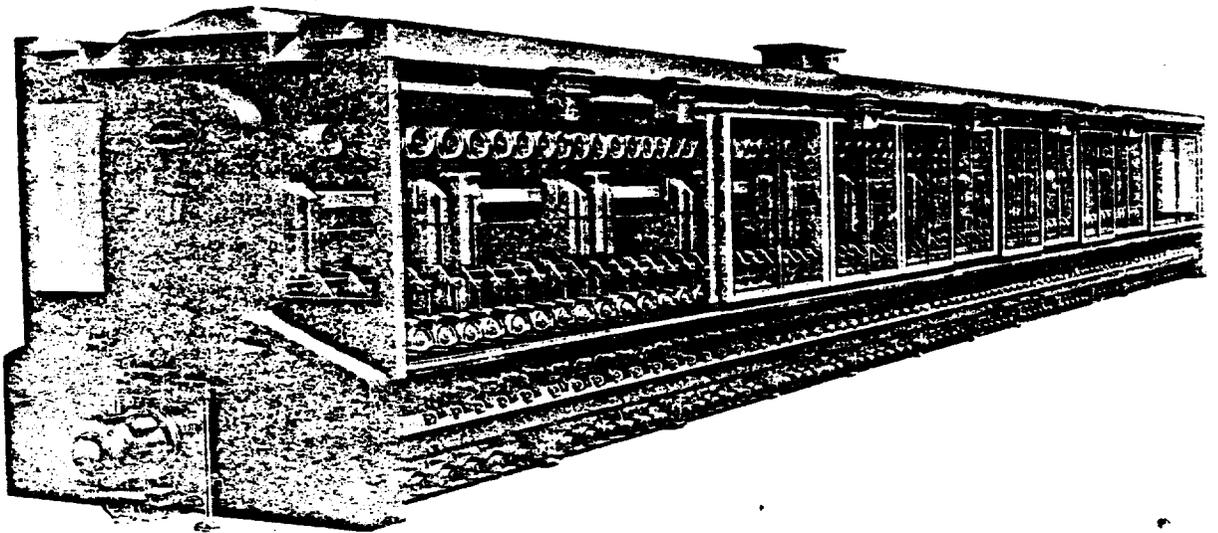


FIG. 59.—A centrifugal (Topham Box) Viscose Rayon Spinning Machine.

for the degree of stretch to be kept constant and to be the same from spindle to spindle. Differences in tension greatly affect the lustre of the yarn.

Fig. 65 shows a doffer removing a cake from a Topham Box; several other cakes already removed may be seen standing on the table.

Purification. The yarn collected in the Topham Box is impure and relatively weak; it has to be purified. Purification consists of four operations, *viz.*, (1) washing; (2) desulphurising, a process which is sometimes called sulphiding; (3) bleaching; (4) washing.

At one time the yarn was wound into skeins, and these were washed, sulphided, bleached and washed, and then re-wound on to bobbins or cones. These operations were carried out with the hanks suspended from ebonite-covered rods, which as they were carried down a long machine were sprayed with the purification liquors. It is, however, a costly operation to wind yarn into skeins and then re-wind it, and an operation, moreover, that requires highly skilled and practised operatives.

Nowadays it is more usual to carry out the purification with the yarn still in cake form, and this effects a considerable economy, besides avoiding the possibility of damage (hairiness due to broken filaments) that is likely to occur in skein-winding and backwinding. The cakes are mounted on perforated spindles, as shown in Fig. 66, and the purification liquors are fed to the spindles and forced through the cakes.

The first wash is with water; the second is with sodium sulphide solution to remove sulphur, and possibly compounds of sulphur, residual from the xanthate. The yarn is still not quite white, so it is next treated with a slightly alkaline solution of sodium hypochlorite to bleach it; this is followed by a wash with dilute hydrochloric acid and a final wash with water. The cakes are then dried.

Owing to the improved quality of the wood-pulp that is available, it has been found possible in some cases to cut out the hypochlorite bleach, and a considerable proportion (although probably not the bulk) of viscose rayon is not bleached at all.

Again, some manufacturers purify their cakes without taking them out of the pots. The full pot is removed from the spinning machine, and is rotated and simultaneously sprayed with the purification liquors, which leave the pot through the perforations in its sides.

Textile Processing. Some consumers will take delivery of viscose rayon in cake form, and twist directly from the cakes. For others it is first wound on to cheese, cone, or bobbin before despatch.

Bobbin Spinning. Not all viscose rayon is collected in cake form

in the Topham Box. Some is wound, without twist, on to spools or bobbins with perforated barrels. These are then put in a pressure-dyeing type of machine, and the purification and bleaching carried out with the yarn on the perforated bobbins. Finally, the yarn is dried, and then oiled, twisted and wound on to ordinary bobbins for despatch.

CONTINUOUS SPINNING

Three ways of purifying viscose have been described: (1) in hank form, the hanks having been wound from the cakes in which the viscose was spun with twist; (2) in cake form with twist in the yarn; (3) on perforated bobbins without twist. Clearly methods (2) and (3) represent a great saving of labour compared with method (1), for in this last method the hand-winding and subsequent backwinding from hank to cone or bobbin are expensive in labour and therefore in cost. At one time all viscose was purified in hank form, but to-day more and more viscose is being purified in cake form. All these three processes are, however, discontinuous or batch processes, and usually manufacturers prefer for any process a continuous rather than a batch method. Usually a continuous process is well suited to a large production at an economical cost. If viscose rayon has to be collected in cake form, wound into hanks, given several wet processes of purification and then re-wound on to cones or other packages for textile use, such processing will involve heavy labour costs. If the process is shortened by treatment of the yarn in cake form, much is saved, but still each cake has to be handled, put in a pressure purification plant, treated, taken out and as a rule re-wound. Considerable labour is still involved, and the manufacture of viscose rayon even by this method is a process much more complicated than the dry spinning of cellulose acetate. Accordingly, various methods have been devised for continuous processes in which viscose could be extruded, purified, dried and wound in the first instance on a bobbin on which it could be supplied to textile manufacturers. Those processes which have reached production dimensions are:

1. The Nelson Process which Instrafl Ltd. announced in 1947 that they had been operating for some years. The sole licence for the manufacture and supply of the machinery for this process to all countries except N. and S. America and the U.S.S.R. has been acquired by Dobson and Barlow Ltd., to whom I am indebted for much of what follows regarding this process.
2. The Industrial Rayon Corporation of America process.
3. The Filamatic, a process announced by the American Viscose Corporation.

The Nelson Process

The cardinal difficulty in the continuous spinning of viscose is that the wet treatments which it has been usual to give to viscose spun into cakes have occupied considerable time. If, for example, viscose were spun at a speed of 70 metres per minute and it required 30 minutes (washing, bleaching, etc.) to purify it, then a run of 2,100 metres—more than a mile—would be required in which to give the treatment. Floor space has to be kept within reasonable confines. In the Nelson Process three factors contribute to keep the floor space within very reasonable confines. They are:

1. The method of presentation of the yarn to the treating liquors. It takes very much less time to wash a single end of yarn than it does to wash a large hank or cake. This single factor may cut down the time necessary for purification to one-tenth of what would otherwise be required.
2. The desulphurising and bleaching processes are omitted, so that the only treatment the yarn has to undergo is (a) completion of the coagulation process which started as soon as the yarn was extruded, (b) removal of the acid liquors from the yarn by washing, (c) drying.
3. The use of thread storing and thread advancing rollers.

Elimination of Desulphurising. The elimination of the desulphurising process (treatment with sodium sulphide) was the crucial step in the development of the process. Long ago it was known that if sulphur (and possibly some sulphur compounds) was left in viscose rayon and the usual sodium sulphide desulphurising wash omitted, yarn of dull or subdued lustre was obtained; this method was, in fact, one of the earliest used for making delustred yarns. It was at first suspect on the grounds that sulphur or sulphur compounds left in the yarn would oxidise to sulphur dioxide or sulphur trioxide and that the sulphurous and sulphuric acids so formed would tender the yarn or fabric. In the Nelson Process it is found that the sulphur residual in the viscose rayon is usually from 0.2 to 0.3 per cent, although it can be kept down to 0.1 per cent. There is no tendering, not even if much larger quantities of sulphur are left in the viscose rayon. Evidently the early fears that residual sulphur would cause tendering were groundless. Nearly all fabrics made from rayon receive some wet treatment for de-sizing, scouring or dyeing purposes and in any such process the residual sulphur in Nelson Process viscose rayon is removed, so that there is nothing to fear in this respect. Very occasionally, fabrics are woven for use, e.g., in upholstery, in the loom state, *i.e.*, they receive no wet processing and in these rela-

tively rare cases, Nelson Process viscose might not be suitable unless the yarn were given a scour before weaving.

Elimination of Bleaching. Once the decision to omit the desulphurising process had been taken, little difficulty was foreseen in omitting the bleaching. Actually, too, considerable quantities of cake-spun viscose rayon are not bleached. This has been made possible by the improved quality of the wood-pulp available, and by the fact that if it is necessary to obtain really perfect whites, then the viscose rayon can be bleached in fabric form. The decision to omit the desulphurising and bleaching processes clearly cut down the time necessary for the purification of viscose rayon to a fraction of what would otherwise have been necessary. Even so, if we assume that, as a result of the presentation of the yarn in single-end form and of the omission of these just-discussed processes, the time of treatment is reduced from, say, thirty minutes to two minutes, a considerable problem still remains. In two minutes a machine spinning at 70 metres per minute will produce 140 metres of yarn. How is this to be disposed during the purification processes? The answer is in the case of the Nelson Process is by the provision of thread storage and thread advancing rollers.

Thread Storing and Advancing Rollers. The thread storing and thread advancing rollers are the essential feature, the heart of the Nelson Process. They consist of two rollers skew to each other, as shown in Fig. 67. The yarn passes round these rollers more than 100 times, and, as the diameter of the rollers is $6\frac{1}{2}$ in.—which corresponds to a circumference of nearly 20 in.—the time taken to make this journey, even if the rollers were close together, would be about one minute at a speed of 70 metres per minute; because, as is shown in Fig. 68, the rollers are some distance apart, the time taken by the yarn to pass from one end of the rollers to the other is between two and three minutes. Here, then, is a solution to the problem of purifying viscose rayon as it moves continuously from coagulating bath to take-up bobbin in a reasonable space: by "storing" the continuously moving yarn on

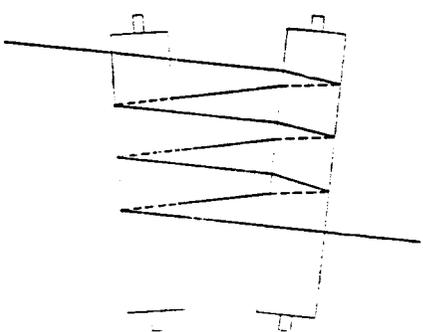
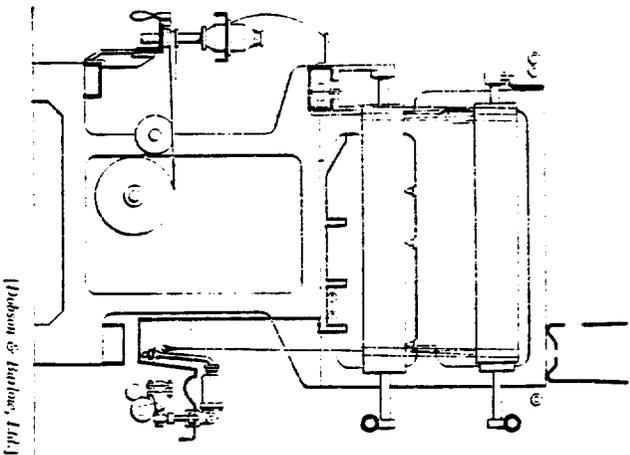


FIG. 67. Showing how two rollers skew to each other cause a thread to advance along them.

two rollers, a length of time running into minutes is provided for the purification process. The rollers are each 3 ft. 8 in. wide, and are made of ebonite, except for the drying end, which is of corrosion resistant metal. Note that the spiral passage of the yarn along the roller is achieved by having two rollers a little out of parallel, as shown (exaggerated) in Fig. 67. In the Nelson Process the two rollers are a little out of parallel in two planes.



(Nelson & Taylor, Ltd.)

FIG. 68.—Diagrammatic sketch of the Nelson Continuous Rayon Spinning Machine.

Note filaments emerging from coagulating bath at right-hand side, passing round the thread-advancing rollers, and being taken up as dry yarn on the bobbin at the left.

Manufacture. The viscose is metered by a pump through a filter and through the spinnerets which are submerged in a lead-lined tank containing the usual coagulating liquor. The thread emerges at right angles to the surface of the bath, and is drawn up almost vertically to the top roller; it descends to the bottom roller and travelling round the lower half of its circumference, returns to the top roller. During the process it advances itself along the axes of the rollers (due to the slight inclination of the axes of the two rollers towards each other), and in this manner travels around the rollers and across the machine from the wet side to the dry side. The standard machine has forty-eight spindles and is 45 ft. long and 6 ft. wide. The rayon is spun on one side of the machine, called the "wet

side", and by its journey along the tilted rollers reaches the "dry side"; it passes on the rollers across the width of the machine. During the first fifty turns round the rollers (about 75 metres of yarn) coagulation is completed, partly by acid carried by the yarn from the bath, partly by acid sprayed on to it on the roller; in the next thirty turns the yarn is washed with two jets of water directed on to the top surface of the lower roller. The yarn now passes to the metal section of the rollers, which are electrically heated, so that in another thirty turns the yarn is dried. In 110 turns the yarn travels about 165 metres, so that if the spinning speed is about 70 metres per minute it takes the yarn nearly two and a half minutes to pass from coagulating bath to take-up bobbin. On leaving the drying section of the rollers the thread is guided over an oiling device, then through a lappet, and down to a cap-spinning or ring-spinning bobbin. The cap bobbin holds 12 oz., the ring bobbin 3-3½ lb. yarn. This process is an elegant solution of the problem of continuously spinning viscose, and is being extensively adopted by some of the leading spinners. It has already been used on a large scale, and gives a good product which can be made into the finest fabrics.

The Yarn Spun. In practically every respect continuous spun viscose rayon is similar to that spun by the older methods. Because the viscose emerging from the spinneret is converted into a thread which is not again touched by hand until it is dry, it is claimed that the quality is greatly improved and that this results in fewer warp breaks in weaving and in comparative freedom from bright picks, bars and stripes in the finished fabric.

A stretch can be applied by having a reduced diameter on the end of that roller to which the thread passes directly from the spinning-bath: as the thread next passes round the normal diameter of the roller, it is stretched. Yarn of 2-filament denier with a tenacity of 2.5 grams per denier and an extension at break of 20 per cent can be spun.

The most important physical difference from batch-treated yarn is that Nelson Process yarn, having been dried unrelaxed, shrinks on re-wetting; an allowance of 4 per

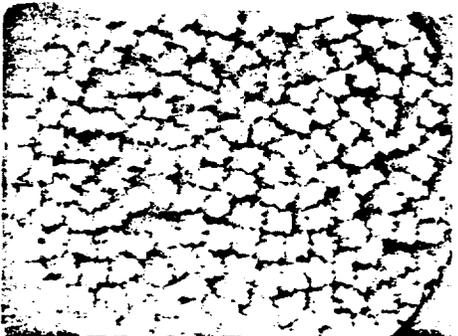


FIG. 69.—75 denier 19 fil viscose rayon spun by the Nelson Continuous Process.

(Thomson, Ltd.)

cent must be made for this in respect of expected cloth widths, warp lengths, hosiery lengths, etc. Fig. 69 shows a cross-section of viscose rayon spun by the Nelson Process. The filaments are uniform and normal for viscose rayon (compare Figs. 79, 80).

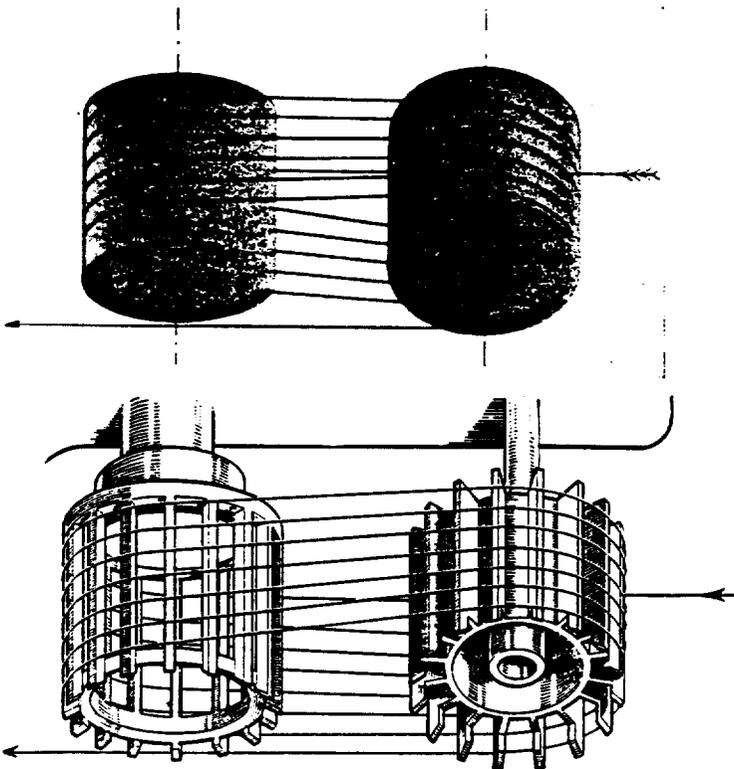


Fig. 70.—A diagrammatic representation showing the principle of the advancing thread by two reels set eccentrically.

Fig. 71.—Two cages (a sprocket above and a spider below) set eccentrically will also advance the yarn.

The Industrial Rayon Corporation Process

The Industrial Rayon Corporation of America have developed and successfully operated a continuous-spinning process for viscose rayon. The same problem—viz., providing sufficient time for the purification of the rayon—had to be solved. Their method was to store the continuously moving yarn on helical reels. These are small and made of moulded plastic materials which resist the attack of the chemicals used in the spinning process. Each treatment can

be isolated on one or more small advancing reels. The advancing helical reel was first suggested in some German patents as early as 1910, was then forgotten for a long time, was taken up again in America in connection with the spinning of cuprammonium rayon and finally adopted and used successfully for viscose rayon by the Industrial Rayon Corporation.

The Thread Advancing Reel. The thread advancing reel, which is the "heart" of the Industrial Rayon Continuous Spinning System, consists of two skewed reels, one inside the other. The principle on which it works is as follows: If a belt passes round two pulleys that are skewed to each other, the belt worms its way off as they rotate; similarly, yarn passed round the pulleys travels or advances along them (Fig. 70). If reels or cages are used instead of pulleys, as shown in Fig. 71, the yarn still travels along them. If now one cage is placed inside the other, skewed, the thread advancing reel is made (Fig. 72).

The Industrial Rayon Corporation started their plant at Painesville, Ohio, in 1938; the introduction of this process marked a revolutionary change in the methods of spinning viscose in America, although even at that date Lustrafil Ltd. were already using the Nelson Process in this country. World rights (excluding U.S.A. and South America) of the Industrial Rayon Process have been purchased by Courtaulds, Ltd., who have built a factory in which Industrial machines have been installed.

The preparatory processes used are those common to all viscose plants, but as the yarn emerges from the coagulating bath it is drawn

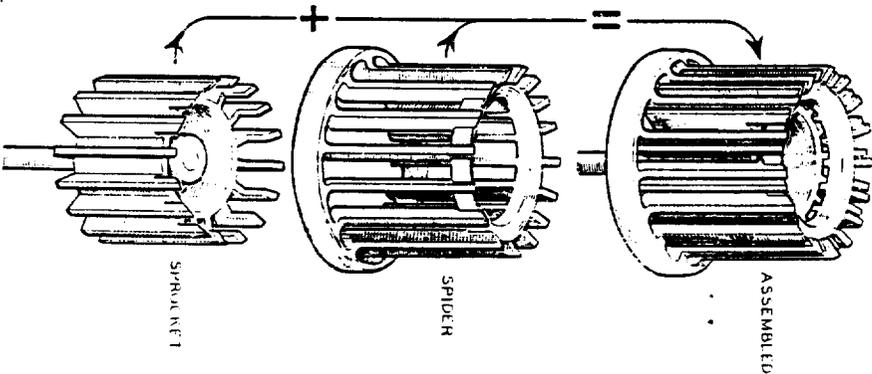


Fig. 72. Diagram showing how the sprocket fits into the spider on an eccentric axis to form the complete thread advancing reel.

at that date Lustrafil Ltd. were already using the Nelson Process in this country. World rights (excluding U.S.A. and South America) of the Industrial Rayon Process have been purchased by Courtaulds, Ltd., who have built a factory in which Industrial machines have been installed.

up to the first of the thread advancing reels, on which the yarn after many revolutions is advanced from the back to the outer end, and then falls to the next section, in which eight more advancing reels (made of plastic) carry the yarn through a like number of processing treatments for washing, desulphurising, bleaching and conditioning. The arrangement is shown diagrammatically in Fig. 73. Note that whereas the Nelson Process omits the desulphurising and bleaching processes, the Industrial Rayon Corporation Process includes them. The treating liquors are applied through glass tubes placed immedi-

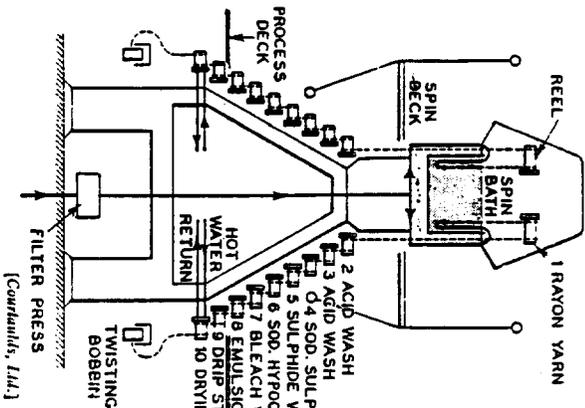


FIG. 73.—Diagrammatic arrangement of Industrial Rayon Corporation Continuous Spinning Process.

Note that the filaments are formed in the coagulating bath at the top of the picture, and work their way downwards round ten thread advancing reels to be taken up (dry) on the twisting bobbin at the bottom of the picture.

ately above the individual reels, so that the liquor flows on to the yarn as it passes over the surface of the reels in a single layer. As a result, every inch of every filament receives the same uniform treatment. Finally the yarn passes to an aluminium drying reel which is internally heated with hot water or steam; then the dry yarn is cap-twisted on to plastic bobbins which hold about 3 lb. yarn. It is then ready for shipping. During the process the yarn has passed round ten reels; its time of processing is five and a half minutes, and more than 400 metres of yarn is travelling between jet and bobbin at the spinning speed, which is probably of the order of 80 metres per minute. Each machine has 200 spindles; it has three operating levels, whereas the Nelson Process is operated entirely from floor

level. The Industrial Rayon machine is double-sided, the Nelson is single-sided.

The quality of the yarn produced by the Industrial Rayon Corporation Process is very good, and especially it contains relatively few knots and broken filaments. Before the 1939-45 War this process was producing 9,000 tons per year of viscose rayon; during the War the production was largely diverted to 1,100 denier high-tenacity yarn for tyre cord. The stretch necessary to give the high tenacity was applied by merely changing the gear ratio of two of the ten thread advancing reels. The process is in operation under licence throughout the world.

Conclusion

It seems clear that two processes of spinning viscose continuously have shown themselves satisfactory. A huge production of viscose yarn has been made by them, yarn that is claimed to be superior in quality to that made by batch processing. In addition, the Filomatic Process, although not yet publicly described, doubtless makes a third satisfactory process.

It has been reported that the Avisco Filomatic Continuous Spinning Process gives in a matter of seconds a dried and finished yarn of uniform physical properties and dyeing affinity, yarn which is said to be spun at a high speed.

Note that the main differences between the Nelson and the Industrial Rayon Corporation Processes are that the former uses one pair of thread advancing rollers; the latter uses ten single thread advancing reels; the former omits desulphurising and bleaching; the latter includes them.

MECHANICAL CRIMP

There is no need for continuous filaments to be crimped, but staple fibre is made a little more like wool by the insertion of crimp. The usual method is to pass the fibre through fluted rollers or some such device which will crimp it mechanically just before it is cut into staple. The finer qualities of wool such as 70's merino have more crimp than coarser qualities, and a good crimp seems to enhance the quality of any yarn; even coarse wool, straight and free from crimp, has been crimped to make better carpets.

About 1939 it was observed in Japan that when viscose rayon was spun into a coagulating bath which was not, by ordinary standards, strongly enough acid, the viscose filaments were finely crimped. The process has been developed well and to-day most of Japan's

staple viscose is sold chemically crimped. If the spinning coagulation bath contains 120 grams per litre of acid, the filaments are normal and do not crimp, but if the acid content is only 90 grams per litre then the filaments show a fine crimp; if the acid is reduced to 70 grams per litre they show a lot of crimp. In order, therefore, to make the crimped yarn, the viscose is spun into a bath with a low acid content and a high salt content. The coagulated filaments are immediately stretched 40 to 50 per cent in a second bath at 90° C., they are stretched a little more in air as they leave the bath, and are then squeezed and cut into staple. The fibres are still straight, but when wetted further by immersion in water they crimp. Then they are dried under tension but crimps on wetting.

When the fibres that crimp are examined it can be seen that they are asymmetrical; all the serrations are on one half of the filament and the *skin* on this half is thinner than on the nearly smooth half (Fig. 74). It is the asymmetry that is responsible for the crimping but the mechanism of the formation of the asymmetry is less clear; it has been suggested that the reduced acid concentration retards the

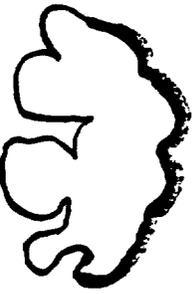


Fig. 74.—Cross-section showing asymmetry of "chemical crimp" fibre.

decomposition of the xanthate, but that the dehydration and coagulation of the viscose which are brought about mainly by the salts, which are high in concentration, in the bath proceed at their usual speeds. The coagulation process causes a skin to form round the filament whilst decomposition is incomplete; decomposition goes on and the products of it burst the skin at one side; coagulation and serration start again

but the viscose is already too far decomposed to do more than form a very thin skin. This results in a fibre with one half nearly smooth in section and covered with a thick original skin (top half of Fig. 74) and with the other half serrated but with the thinnest of (secondary) skins (lower half of Fig. 74).
When a fibre is wetted it swells, and when a fibre with thick skin on one side and thin skin on the other is wetted, it will, if free, coil in such a way that the thick skin is on the inside of the coil—on the inside because it swells less than does the thin skin. If held more or less straight in yarn or fabric form it is not free to coil, but makes the first movement to do so, and this results in crimp. The two factors which contribute to the crimping power are (1) the asymmetry of the serrations, (2) the irregularity of the skin thickness—the filaments

are called "broken-skin filaments"; either will give crimp if produced alone, ordinarily the two causes of asymmetry are produced simultaneously.

There is another way of producing skin asymmetry which also gives a crimping fibre. This is by making "conjugate filaments", spun from a special jet (Fig. 75) wherein two different viscose solutions, one young and one old, are deliberately combined to give a filament with one side made from young and the other from old viscose. The young viscose gives a thick skin and the old viscose a thin skin. In Fig. 75 young viscose is fed into space C on one side of the dividing septum B, and old viscose is fed into D; both are squeezed side by side through the spinneret hole A; there is no turbulence, but only viscous flow so that the two solutions emerge side by side from the same spinneret.

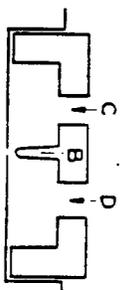


Fig. 75.—Type of jet used for making conjugate (crimping) filament.

This principle is the basis of the method used for making Orlon Sayelle, an acrylic fibre which develops a spiral crimp when finished (p. 568).

SARILLE

Sarille is a crimped viscose staple made by Courtaulds; its aim is to produce wool-like fabrics, but with its cellulose structure it cannot proceed very far along this path. It has been used for dress fabrics with a full soft handle. In the knitwear trade it finds its way into interlock and double jersey. The success of the candlewick bedspreads that are made out of rayon staple has been attributed to Sarille. The crimp is due to asymmetry of structure of the fibre and is permanent in the sense that it will reassert itself in the absence of tension. If maximum relaxation of fabrics made from Sarille is allowed, the crimp exerts its full action, shrinking the fabric and making it bulky. Shrinkage should be about 10-12 per cent, and accordingly fabric must be woven sufficiently wide to allow for this. Sarille is usually spun on the cotton system; the coarsest filament denier possible for the required yarn counts should be used in order to yield crispness and voluminosity. For example, a 3-denier 2-inch staple can be spun into a 22's (cotton counts, *i.e.* 240-denier) yarn. Very often the manufacturer of man-made fibres has his eye on the uses to which wool is put—how fine to make a "woollen" pullover or cardigan or dress out of cellulose or polyacrylonitrile. The purchasing public is perhaps not so discriminating as it once was.

CHAPTER II CELLULOSE ACETATE

CELLULOSE is chemically stable; its derivatives are not easily made, and it was not until 1869 that its acetate was prepared by Schützenberger, who made it by heating cellulose with acetic anhydride in a sealed glass tube. In 1894 Cross and Bevan showed that the action proceeded readily at atmospheric pressure if either sulphuric acid or zinc chloride was present to act as a dehydrating catalyst. Using this method they obtained a cellulose triacetate, and found that it was soluble in chloroform.

It was discovered, in 1903, that if the cellulose triacetate is partly hydrolysed back to a stage half-way between the triacetate and diacetate, it loses its solubility in chloroform, but becomes soluble in acetone, which is a much more convenient solvent to use. If, however, cellulose is directly acetylated in the first place to the 2½-acetate stage it is not acetone-soluble (*cf.* p. 296).

In the 1914–1918 war aeroplanes had fabric wings, and it was found that if they were coated with a solution of cellulose acetate in acetone they tightened up and became impervious to air. The cellulose acetate was manufactured in Switzerland by the brothers Dreyfus, and as their supplies were inadequate to treat the aeroplanes of all the Allies they were asked to come to England to start a factory for the manufacture of cellulose acetate in large quantities. This they did at Spondon, near Derby.

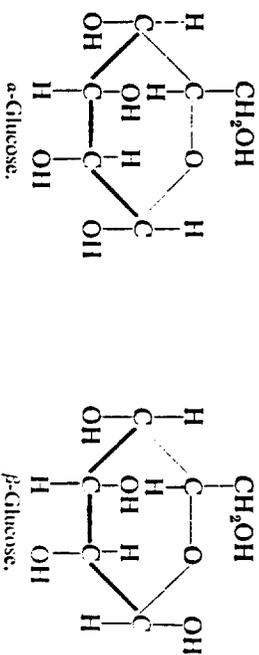
When the war ended in 1918 there was a very large production of cellulose acetate coming from the Spondon factory, but no demand for it. After a period of intensive research carried out under the inspiring leadership of Dr. Henry Dreyfus, a method of converting it into artificial silk was discovered, and by 1921 this fibre was marketed as "Celanese". In 1924 an allied company was also making and selling it in America. Since the 1957 merger of British Celanese with Courtaulds, ordinary acetate has not been quite so much to the fore in the U.K. Nevertheless, ordinary acetate has one of the most beautiful handles in the world of fibres. It is making great strides in Japan (in 1964 they made 70 million lb.) and, unexpectedly, in Chile. In America it is manufactured and sold as Celanese by the Celanese Corporation of America, as Estron by the Tennessee Eastman Co., as "acetate" (the generic term) by the Pont de Nemours and Co., and as Seralacta by the American Viscose

Corporation. Very large quantities of the order of 50 million lb. per year have also been made by the Rhodiacta firms in Europe, notably in France and Germany. Acetate fibre is also produced under the name Aceta by Farbenaßwerken Bayer: it was previously made under the same name by the former I.G. Farbenindustrie. One of the earliest and best spinners of acetate yarn was Lansil Ltd. of Lancaster; they still make it, but are no longer independent, having been taken over by Monsanto of America in 1962.

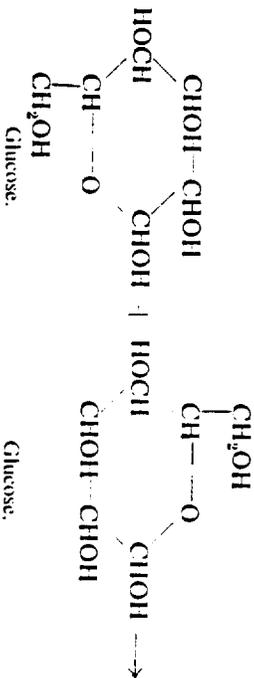
Chemical Constitution

The long-chain molecule which forms the basis of cellulose acetate is cellulose, the abundant natural polymer. It is the same basis as is used for viscose and cuprammonium yarns, but in the case of cellulose acetate most of the hydroxyl groups have been acetylated.

The unit from which cellulose is built up is the glucose molecule. Two stereo-isomeric forms are known, α - and β -glucose, but only the latter is a building-brick of cellulose. The constitution of glucose is:



Two molecules of β -glucose will combine to give one molecule of cellobiose:



increasingly for the manufacture of cellulose acetate, but in Russia cotton is still the main raw material for cellulose acetate.

The chemicals needed are: (1) acetic acid, which nowadays is frequently made by catalytic oxidation of alcohol, (2) acetic anhydride, which is made by dehydrating acetic acid at high temperatures to give ketene:



and then passing the ketene into more glacial acetic acid with which it combines to form acetic anhydride:



and (3) acetone. The cracking of petroleum yields large quantities of isopropyl alcohol, some of which is oxidised to acetone. In addition, sulphuric acid is needed, and a good supply of water. The water, and in fact all the chemicals used, must be substantially free from iron.

The stages in the manufacture of cellulose acetate rayon are as follows:

Cotton Purification. Cotton linters—fibres too short to be spun—are purchased in bales. The bales are broken and the linters kier-boiled under pressure for from four to ten hours with an alkaline liquor, which may be a solution of either sodium carbonate or caustic soda, or a mixture of the two. They are then rinsed, washed, bleached with sodium hypochlorite, washed and dried.

Pre-treatment. The purified cotton is steeped in glacial acetic acid to make it more reactive so that it will acetylate readily.

Acetylation. The pre-treated cotton is loaded with an excess of glacial acetic acid and acetic anhydride into a closed vessel fitted with a powerful stirrer. Suitable quantities are:

- 100 lb. purified linters (air-dry weight).
- 300 lb. acetic anhydride.
- 500 lb. glacial acetic acid.

These are thoroughly mixed together, but as yet no chemical reaction takes place.

When the mixing has been accomplished, 8–10 lb. of sulphuric acid dissolved in about eight times its own weight of glacial acetic acid is added. The sulphuric acid reacts with the acetic anhydride to form sulpho-acetic acid, which is the real acetylating agent.

Acetic anhydride and acetic acid would only acetylate the cellulose very slowly indeed—far too slowly for commercial practice—without the sulphuric acid. Sometimes the sulphuric acid is described as a catalyst, and in the sense that it promotes the reaction—*i.e.*, the esterification of the cellulose—the description is justified; on the other hand, the quantity of sulphuric acid used is considerable when compared with the weight of cellulose that is acetylated, and, furthermore, the sulphuric acid is consumed in the reaction; in these respects the sulphuric acid may more properly be regarded as one of the reagents than as the catalyst of the reaction.

The acetylation reaction is powerfully exothermic; it is desirable to keep the temperature low in order to avoid undue degradation of the cellulose—*i.e.*, to avoid, so far as possible, the breakdown of the long-chain cellulose molecules into shorter molecules of degraded cellulose. Consequently the acetylation vessels have to be cooled.

For the first hour of the reaction the temperature is kept below 20° C., and for the next seven to eight hours at 25–30° C. The mass becomes gelatinous and very viscous. At the end of about eight hours all the cellulose will have been converted into cellulose triacetate—*i.e.*, the cellulose will have been completely acetylated.

Samples are continually taken from the mass and examined, so that it can be known when this point has been reached. The indications that acetylation is complete are:

1. The fibres have all dissolved; a sample examined under a low-power microscope no longer shows (as it does in the early stages of the reaction) swollen but undissolved fibres.
2. The sample is completely soluble in chloroform, which is a good solvent for cellulose triacetate. (Note, however, that it is not a solvent, although it is a powerful swelling agent, for the secondary or commercial cellulose acetate.)

The degradation that the cellulose has undergone during acetylation can be assessed by measuring the viscosity of a solution of its ester. The cellulose triacetate which is formed by the direct acetylation of the cellulose, as described above, is known as "primary" acetate.

Hydrolysis. In order to convert the chloroform-soluble primary acetate into the acetone-soluble secondary acetate it is run, together with the excess acetic acid and anhydride, into water so that a 95 per cent solution of acetic acid results, and allowed to stand for twenty hours at a higher temperature. Acid hydrolysis takes place, and an acetone-soluble product results. Samples are removed and tested at intervals, so that the reaction can be stopped when the acetyl con-

tent has been reduced by the desired amount. When this is the case, the whole mixture is poured into excess of water, which so dilutes the acid that it will no longer hold the cellulose acetate in solution, and a precipitate of chalky flakes of cellulose acetate is formed, and the secondary acetate. The degree of polymerisation is formed. This is 350-400. The liquors which contain acetic acid are conducted to a recovery plant, where the acid may be extracted from the water with a solvent—*e.g.*, cresol. The secondary acetate is thoroughly washed, centrifuged and dried at a low temperature. The product from each batch is tested for viscosity, ash, and acetyl content, and every care is taken to blend different batches with each other. Blending—at every stage in order to ensure, as far as possible, that a uniform product results, and that finally the yarn may be mixed and woven without showing differential effects of lustre or dyeing affinity.

It is important to note that during the hydrolysis stage any mixed ester—*i.e.*, cellulose acetate sulphate (often called sulpho-acetate)—has the sulphate radicals removed. In the early days of making cellulose acetate rayon the importance of freeing it from combined sulphuric acid was not fully appreciated, and when rayon containing combined sulphuric acid was stored, after a time sulphuric acid was slowly liberated, and degraded the rayon. In addition, the presence of sulphuric acid in the rayon alters the dyeing affinity. Cellulose acetate rayon to-day is for all practical purposes free from combined sulphuric acid.

Preparation of Dope. The secondary acetate blended from many batches is mixed in a closed vessel with a powerful stirrer with about three times its weight of acetone. It dissolves slowly, and after twenty-four hours it will be completely dissolved. If a dull yarn is required, titanium oxide will be added at this stage, and if a spun black pigmented yarn is required, black pigment will be added. The product from several of these solution vessels is again blended in a mixing-tank, and the dope (the name used for the solution of the cellulose acetate in acetone) if it has not been pigmented is white and viscous. It is filtered and de-aerated, and then run into a feed-tank. The dope contains 25-35 per cent of cellulose acetate and has a high viscosity.

Spinning. Dope is fed from the feed-tank through pipes to the spinning cabinets (Fig. 95). A metering pump ensures that a constant flow (so many grams per minute) of dope is fed to the spinning jet, but between the pump and the jet is a candle-filter to give a final filtration and avoid trouble due to solid particles interfering with the smooth flow of dope through the jets. The spinneret consists of a

metal plate through which a number of small holes, perhaps 0.03 mm. in diameter, have been drilled, usually concentrically. The number of holes in the jet determines the number of filaments in the yarn; if the number in a 150 denier yarn is sixty, the filament denier will be 2.5; if it is thirty the filament denier will be 5. The same total denier—*i.e.*, yarn denier of, say, 150—is often spun in a variety of different filament deniers; very fine filaments are desirable for some purposes, coarser for others. As the dope is squeezed out of the jets (Fig. 96) it emerges into the spinning cabinet and travels vertically down this a distance of from 2 to 5 metres to a feed-roller, from which it is guided on to a bobbin. If the bobbin is a cap-spinning bobbin, twist is inserted in the yarn as it is taken up; if, for example, the spinning speed is 300 metres per minute and the bobbin is rotating at 10,000 r.p.m. a twist of $\frac{10,000}{300} \times 39.7 = 0.76$ turn per inch will be inserted. Take-up speeds are normally between 200 and 400 metres per minute. Advantageously, a slight stretch will be imparted to the yarn in its draw-down from the jet; this imparts some degree of orientation to the molecules and yields filaments of strength greater than they would otherwise have. The diameter of the filament as taken up on the bobbin is therefore dependent on three factors: (1) the rate at which dope is fed by the pump, (2) the diameter of the jets, (3) the rate of draw-down. In the cabinet, hot air is fed in near the bottom at a temperature of 100° C.; this evaporates practically all the acetone in the dope emerging from the

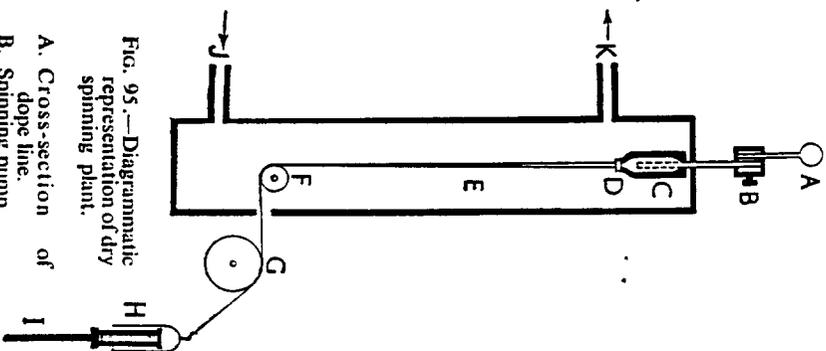


Fig. 95.—Diagrammatic representation of dry spinning plant.

- A. Cross-section of dope line.
- B. Spinning pump.
- C. Filter candle.
- D. Jet.
- E. Spinning cabinet.
- F. Guide roller.
- G. Take-up roller.
- H. Cap and bobbin.
- I. Bobbin driving spindle.
- J. Hot air inlet (100° C.).
- K. Air and acetone vapour outlet (80° C.).

metal plate through which a number of small holes, perhaps 0.03 mm. in diameter, have been drilled, usually concentrically. The number of holes in the jet determines the number of filaments in the yarn; if the number in a 150 denier yarn is sixty, the filament denier will be 2.5; if it is thirty the filament denier will be 5. The same total denier—*i.e.*, yarn denier of, say, 150—is often spun in a variety of different filament deniers; very fine filaments are desirable for some purposes, coarser for others. As the dope is squeezed out of the jets (Fig. 96) it emerges into the spinning cabinet and travels vertically down this a distance of from 2 to 5 metres to a feed-roller, from which it is guided on to a bobbin. If the bobbin is a cap-spinning bobbin, twist is inserted in the yarn as it is taken up; if, for example, the spinning speed is 300 metres per minute and the bobbin is rotating at 10,000 r.p.m. a twist of $\frac{10,000}{300} \times 39.7 = 0.76$ turn per inch will be inserted. Take-up speeds are normally between 200 and 400 metres per minute. Advantageously, a slight stretch will be imparted to the yarn in its draw-down from the jet; this imparts some degree of orientation to the molecules and yields filaments of strength greater than they would otherwise have. The diameter of the filament as taken up on the bobbin is therefore dependent on three factors: (1) the rate at which dope is fed by the pump, (2) the diameter of the jets, (3) the rate of draw-down. In the cabinet, hot air is fed in near the bottom at a temperature of 100° C.; this evaporates practically all the acetone in the dope emerging from the

jets, and the acetone-laden air is withdrawn near the top of the cabinet and taken away to a recovery plant, where the acetone may be recovered either by (1) adsorption on active carbon, (2) scrubbing in water-towers, or (3) absorption in a concentrated solution of sodium bisulphite. Efficient recovery of both acetone and acetic acid from the earlier preparative processes is essential for the economical manufacture of cellulose acetate rayon, and in modern

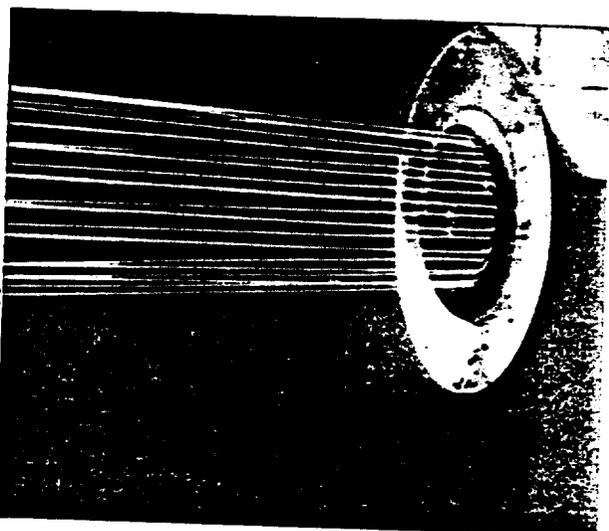


Fig. 96.—Cellulose acetate spinning. As the dope emerges from the spinneret the warm air it encounters evaporates the acetone, leaving individual filaments.

(American Viscose Corporation)

plants the losses are very low indeed. Important factors in the spinning process are the temperature, moisture content and velocity of the air proceeding up the cabinet. Usually a trace of oil—perhaps 1 or 2 per cent—will be applied to the yarn before it goes on to the cap-spinning bobbin, in order to prevent damage to the filaments in winding, and also to prevent electrification.

When the yarn has been collected on the cap-spinning bobbin it is ready for textile use, and this method of spinning, known as "dry spinning", has obvious and considerable advantages in economy of labour over the wet-spinning processes employed for viscose. Per-

haps it is the elegance and simplicity of the dry-spinning process which have most largely contributed to the advancement of cellulose acetate fibres. A single workman can spin more than 200 lb. of acetate silk in his working day.

Subsequently the yarn may have more twist inserted in a separate operation before it is woven or knitted. Some makers supply the yarn on large packages; Farbenfabriken Bayer supply their acetate filament yarn on cones weighing up to 2 kg. and guaranteed knotless. The adoption of large packages is one of the signs of up-to-date processing; large packages mean less labour for package changing, and labour is so costly nowadays that it is well worth spending money on the development of large packages.

Properties

In considering the properties of cellulose acetate rayon, one has to bear in mind that the hydroxyl groups originally present in the cellulose have, for the most part, been esterified. Accordingly, the fibre is less hygroscopic and more water-repellent than viscose. At the same time, its "organic" nature has been increased, and it is correspondingly more prone to swell or dissolve in organic solvents. The esterified condition of the hydroxyl groups caused considerable dyeing difficulties when cellulose acetate rayon was first made, but these have long been largely overcome by the employment of special dyestuffs and the introduction of a method of dyeing from dispersion instead of solution of dyestuffs.

Tenacity. Cellulose acetate rayon has a tenacity of about 1.4 grams per denier and an elongation at break of about 25 per cent. Corresponding figures for wet yarn are about 0.9 gram per denier and 35 per cent. Its water-repellent properties ensure that there is less proportional decrease in tenacity on wetting than is the case with viscose. Up to about 5 per cent increase in length cellulose acetate has a high elasticity, but if it is stretched to higher elongations plastic flow or creep occurs, and the deformation is not fully recovered when the load is released. The stress-strain curves for wet and dry cellulose acetate yarns are shown in Fig. 97.

Resistance to Heat. Cellulose acetate is thermoplastic—i.e., it softens on heating. It melts at about 230° C. with decomposition. If a very hot iron is used to iron fabrics made from it, "sticking" and eventually fusion occur. The acetate decomposes when melted in air, charring taking place. It will burn if ignited, but on account of the simultaneous melting, the spread of combustion is often slow. Cellulose acetate might reasonably be said to offer only a low fire risk, when in bulk. Unfortunately, when used for kiddies' clothing

it is almost as dangerous as viscose or cotton. Research is urgently needed to find a way of making such fibres flameproof. The number of fatal accidents and serious injuries sustained by young children due to "clothes catching fire" is still shockingly high.

Lustre. The lustre is normally bright, but may be subdued by the incorporation of titanium dioxide in the dope. The lustre of bright cellulose acetate is greatly dulled by immersion in boiling water, and reappears on ironing, usually patchily. Care has to be taken not to dull it in dyeing, whilst for ordinary home washing warm water is safest.

Solubility. Cellulose acetate is readily soluble in some organic solvents—for example, acetone, methyl ethyl ketone, methyl acetate, ethyl lactate and dioxan—and is swollen by a large number of others,

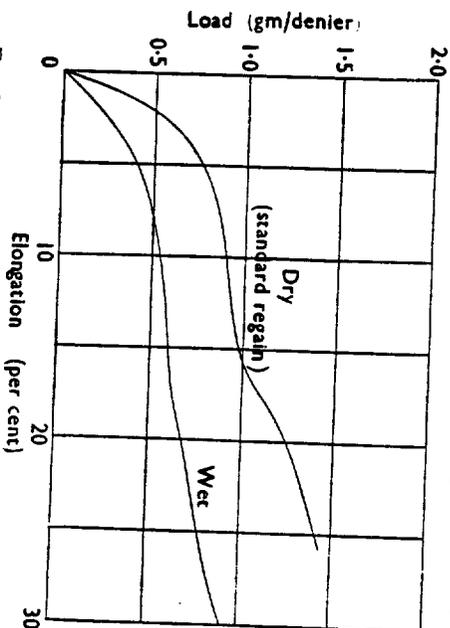


FIG. 97.—Stress-strain diagram of cellulose acetate yarn.

including chloroform, methylene chloride, ethylene chloride and Cellosolve. It is unattacked by ether, which is a suitable extractant for use with it.

Hygroscopicity. The moisture content under standard conditions is 6.5 per cent—considerably less than that of viscose.

Specific Gravity. The specific gravity is 1.32—very similar to that of wool.

Handle. The handle of cellulose acetate is particularly soft, and fabrics made from it drape well. These properties have very largely contributed to its successful development.

Electrical Properties. Cellulose acetate is an excellent insulator. It will readily develop static charges, and for some purposes it is desirable to apply an anti-static finish.

Biological Resistance. Organisms such as moths and mildew find no nutrient in cellulose acetate. Cases of damage are extremely rare, and are invariably due to the organisms feeding on the oil or finishing material applied to the fibre. Cellulose acetate will not produce dermatitis.

Chemical Resistance. Cold dilute acids do not affect it, but concentrated acids—*e.g.*, acetic and formic—attack it in the cold. Alkalis saponify it—*i.e.*, they remove acetyl groups—but dilute solutions up to pH 9.5 are safe.

Resistance to Light. Some tendering takes place when cellulose acetate is exposed to light, but it is usually not very serious; a loss of about 15 per cent in tenacity has been reported after 200 hours' exposure in a Fadeometer.

Morphology. Under the microscope the longitudinal view is that of a smooth featureless cylinder, whilst the cross-section is lobed as shown in Fig. 98.

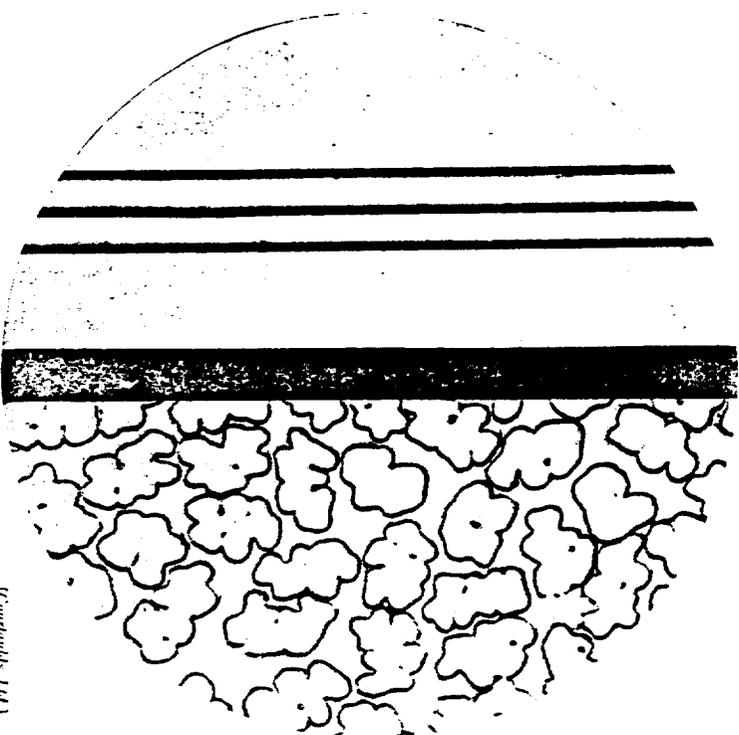


FIG. 98.—Photomicrograph of cellulose acetate filaments ($\times 500$).
[Courtnolds, Ltd.]
Note the lobed outline and the absence of serrations.

CHAPTER 12

CELLULOSE TRIACETATE

TRICEL, ARNEL

The first cellulose acetate that was made was cellulose triacetate, but as it was not soluble in solvents that were then available and were safe to use (see p. 232), it was never made on a big scale in the early days of rayon. Small quantities of about 300 lb. per day of 150 denier cellulose triacetate yarn were in fact spun from a chloroform solution by the Lustron Company in America, starting in 1914 and continuing until 1924, but the process never reached any size. Nevertheless, considering the incomplete knowledge of the chemistry of the product that was then available, and considering also the frightening toxic hazards of using chloroform as a spinning solvent, this production, negligible as it seems to-day, must be rated as a stupendous achievement. Otherwise, until a few years ago all the enormous quantities of cellulose acetate rayon made have been of the secondary acetate.

Lately this position has changed and the manufacture of the triacetate has been carried out on a large scale: Tricel (British Celanese Ltd.) is made in the U.K.; Arnel is made by the Celanese Corporation of America and Trilan by Canadian Celanese Ltd. Courpleta, formerly made by Courtaulds, was discontinued after the 1957 merger with British Celanese. Its properties had been almost the same as those of Tricel. The two main reasons for the development of these fibres are:

1. Solvents for the triacetate which are easy and safe to handle have become available cheaply and in large quantities. Methylene dichloride, which is an excellent solvent for triacetate, but is not a solvent for secondary acetate, has been available cheaply since 1930.
2. The development of the synthetic fibres such as nylon, Orlon and Terylene has shown that there are uses to which a hydrophobic fibre can be put, and that there are many things that can be done with one of these that can never be done with the hydrophilic viscose and (secondary) cellulose acetate rayons and natural fibres.

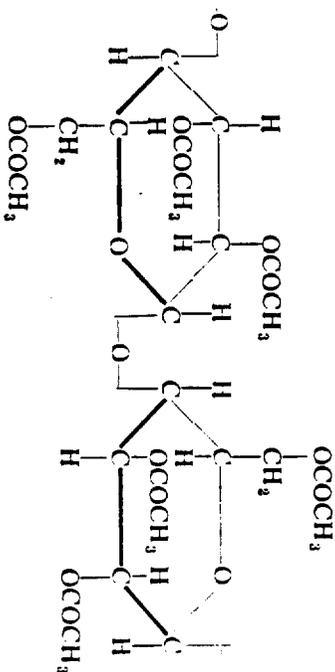
It is mainly this new knowledge which had accrued that has driven the rayon manufacturers to make triacetate: the solvents had been available for long enough.

252

Chemical Constitution

The chemical constitution of the primary triacetate is discussed on p. 234.

It will be sufficient to note here that it is the product of complete acetylation of cellulose and that all of the three hydroxyl groups in each glucose residue are acetylated, whereas in the "secondary" cellulose acetate, with which we have been familiar for forty years, some hydrolysis has been carried out to reduce the number of hydroxyl groups from 3 to about 2.3 per glucose residue. The information already given on pp. 233-235 may be supplemented by reference to the formula:



In this the heavy bonds indicate the nearer edges of the planes in which the flat glucose residues lie. The acetyl groups stand away from these planes so that, in effect, the triacetate fibre molecule consists of a long core of some hundreds of glucose residues lined up serially, and bristling with acetyl side-chains. The core is the same as in viscose rayon, but viscose bristles with hydroxyl and not acetyl groups; the core in secondary acetate bristles with a mixture of acetyl and hydroxyl groups in the ratio of 2.3 : 7. The unit molecular weight of triacetate is 288 and its acetyl value " as acetic acid " is $3 \times 60/288$ or 62.5 per cent; in practice it varies from 61.5 to 62.5.

Manufacture

The raw material is either purified cotton linters or specially pure grades of wood pulp - in either case a pure form of cellulose. The reactivity of the cellulose is enhanced by pretreatment with acetic acid. Two methods of acetylation are available:

1. *Non-solvent process.* The activated cellulose is esterified with acetic anhydride in the presence of a non-solvent such as benzene, which preferably has a slight swelling action on the esterified

cellulose. An acid catalyst such as sulphuric acid, toluene sulphonic acid, or perchloric acid is used; this acid catalyst must subsequently be removed from the fibre by heating in a non-solvent medium with acetic acid, thus purifying the solid cellulose triacetate which is then dried.

2. *Solvent process.* The activated cellulose is esterified with acetic anhydride and acetic acid, using sulphuric acid as a catalyst. Alternatively, methylene chloride can be used instead of acetic acid. When acetylation is complete, all the cellulose fibre will have passed into solution. There is no need to hydrolyse any of the acetyl groups off, as in the preparation of secondary acetate (p. 237), but it is necessary to give a brief hydrolysis to remove combined sulphuric ester groups which, if left in, would make the product unstable. The cellulose triacetate is then precipitated into water, washed and dried.

The fibrous or flake cellulose triacetate is made into a 20 per cent solution in methylene chloride which may contain a small proportion of alcohol. Methylene chloride boils at 42° C. against acetone at 57° C., and as it is dearer, and as there are always some recovery losses, it is likely that cellulose triacetate will be more costly to produce than the normal acetate. Nevertheless, its lower boiling point should effect some economy (less heat) on the dry spinning process that follows. The dry-spun cellulose triacetate fibre is passed over a wick containing an anti-static agent and is collected on cap-spinning bobbins if it is in the continuous filament form. If required for staple, a number of ends are collected into a tow as they leave the spinneret, no twist is inserted, and the tow is crimped and cut to the desired length.

Wet Spinning. Cellulose triacetate is dissolved in glacial acetic acid and this is extruded into either water or dilute acetic acid. Arnel 60 was wet-spun, and it was considerably stronger than ordinary dry-spun Arnel. But it has been discontinued, and probably all of today's triacetate fibre is dry-spun.

Properties

Always the properties of a fibre depend on its constitution, and those of triacetate derive naturally from (1) the cellulosic backbone of its molecule, which gives it the very moderate strength of ordinary rayons and a similar extensibility, and from (2) the forest of acetyl groups which pretty well surround the cellulosic core and which have no liking for water molecules, and consequently make the fibre resistant to water and wet processing, give it a low moisture regain and water uptake and make it less easy to dye. But there is one other property of the fibre which could hardly have been foreseen,

although it derives from its hydrophobic character, and that is that triacetate can be heat-set like the synthetics so that it will hold pleats, that have been deliberately inserted even if subsequently washed, and so that it will resist subsequent creasing. Nowadays the importance that is attributed to thermal setting and dimensional stability is very great. Triacetate shares low production costs with the cellulosic fibres, and highly valued thermal-setting properties with the synthetics, but it also shares their less attractive features: the relatively low strength and durability of ordinary cellulose acetate, and the low moisture regain of the synthetics.

In detail the properties of triacetate are as follows:

Tenacity: 1.2 grams per denier dry (65 per cent R.H. and 70° F.) and 0.8 grams per denier wet. Loop and knot tenacity both 1.0 to 1.1 grams per denier.

Extensibility: 20–28 per cent (standard conditions) and 35–40 per cent (wet).

Initial modulus or load in grams per denier necessary to give a 1 per cent stretch (p. 321): 0.39, the same as ordinary acetate, which should contribute to a good soft handle.

Density: Tricel 1.32 gm./c.c. Ordinary acetate is usually quoted as 1.30, which is practically the same.

Melting point: 290–300° C., much higher than normal acetate (235° C.) both with decomposition. With both fibres there is some softening and sticking when ironed at much lower temperatures, but even so triacetate shows a marked advantage in safe ironing temperatures over ordinary acetate (see Fig. 100). It is noteworthy that the melting point is considerably higher than that of nylon and Terylene which is just over 250° C.

Morphology: Fibres show longitudinal striations, and the cross-section is bulbous (Fig. 101). The difference of appearance between triacetate and normal acetate (Fig. 98) is insufficient for positive identification.

Flammability: Shrinks and melts to a bead when ignited, but will burn and flame, especially if the fabric is of an open structure, such as a voile or nixon—about the same as normal acetate.

Moisture regain: Regain of triacetate at 65 per cent R.H. is 4.5 per cent. (compare nylon 4.2 and ordinary acetate 6.5). All of the natural fibres had high moisture regains; so had viscose and cuprammonium rayons, and ordinary acetate rayon was the first fibre to have a much lower regain. Then came nylon, much lower, and later Terylene and the acrylics with very much lower regains. The trend which one has hoped to see, and which is slowly coming,

NYLON

THE word *nylon* is generic; it is spelt without a capital letter and can be used in the same sense as "glass" to indicate a group of similar materials. An exception to this is provided by some European countries, notably France, where the word Nylon is a registered trade mark of Société Rhodiaca.

Discovery of Nylon. Nylon was a product of the genius of Wallace H. Carothers. This man was a brilliant organic chemist at Harvard University, and forsook the academic life to undertake fundamental research work with the enormous American chemical combine of E. I. du Pont de Nemours & Co., an organisation similar to, but vastly bigger than, I.C.I. in this country. Probably the reasons which induced Carothers to enter industry were the greater facilities, more numerous assistants, greater laboratory space, and the unlimited apparatus and equipment which a large industrial organisation can provide, but which in the 'twenties were not so readily available at a university. Carothers tackled many chemical problems, made many chemical discoveries and it became quite a problem for the du Pont management to find commercial applications for these discoveries. In the first place, the programme that Carothers undertook was one of fundamental research, *without regard for any immediate commercial objective*. Carothers' initial interest was only general polymer research. The fact that some of the newly synthesised polymers were fibre-forming was a surprising and important discovery, but not the objective of the original fundamental research programme. This provides an outstanding example of the good and useful results that can accrue from fundamental research. It was solely with the extension of knowledge of polymer structures as his goal that Carothers started his work in the field of fundamental polymer research—work that led not only to nylon but to neoprene (a synthetic rubber with excellent chemical resistance), to macrocyclic compounds such as the synthetic musks, and to melt spinning itself. Some two years after he started his work Carothers directed his attention particularly to the possibility of finding any product that might be used as a synthetic fibre. He found promise in some polymers known as polyesters, and finally achieved success with other polymers known as polyamides. In 1928, when Carothers embarked on his researches, polymers were not a favourite subject

of study. Chemically, they were infusible, unreactive and insoluble—quite different from the substances the chemist more usually handled. These polymeric substances were intractable, and usually if an experiment produced a substance that was infusible and insoluble it was said to have "failed" and the product was consigned to the waste-bin.

Preparation of Polyesters. Carothers appreciated that these "failures" were much more closely allied to those materials, such as wood, rubber, cotton, wool and so on, that we encounter in our daily lives than are the soluble, small-molecule compounds which the chemist delights to manipulate in his laboratory. Carothers was not only a philosopher, but also an experimentalist, and when given a free hand and practically unlimited resources by his employers, he deliberately set out to make these chemically intractable polymers. He reasoned that just as ethyl alcohol and acetic acid will react with each other to form ethyl acetate, an ester, thus:



so, in a similar way, would a di-alcohol, usually known as a glycol, react with a diacid. Thus hexamethylene glycol would react with adipic acid to form an ester in this way:



Then two molecules of the ester would react to form a molecule twice as long, in this way:



Next, two molecules of this ester would react to give a molecule twice as long, and so on. By building up these condensation products from molecules that had reactive or *functional* groups at either end of the molecule, Carothers prepared some very long molecules indeed. When these were made from glycols and acids they were called polyesters—*i.e.*, polymeric esters—and it was one of these polymeric esters that gave the first promise to Carothers of being a useful fibre. A chemist—his name has never been publicised, but one of Carothers' assistants—dipped a glass rod into a still containing one of these polymeric esters. Doubtless to his considerable astonishment and excitement, the molten material which adhered to the rod as he withdrew it stretched out into a long filament which solidified. Perhaps to his still greater surprise, this filament, even after it was cold,

could be stretched by hand to several times its original length, but, unlike rubber, did not, on release, return to its original length. It is easy to imagine the excitement that must have prevailed in the laboratory on that day, to think of the gratification and satisfaction it must have afforded Carothers to see his reasoning from first principles so convincingly substantiated. Carothers had thought: "Take molecules that can react at both ends, react them and long molecules will result. If the molecules are very long in relation to their other dimensions, they will exhibit fibre-forming properties."

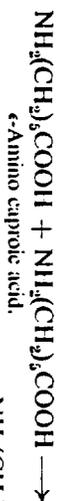
The Introduction of Polyamides. Even so, there was still much hard work to be done. The fibres made from the polyesters were not altogether satisfactory, they were not very strong, and so great were the difficulties confronting the experimentalists that at one time the idea of dropping the work was seriously entertained. Then Carothers with rare insight realised that the solution of the problem lay in the substitution of polyamides for polyesters; these were made, and immediately showed such a big improvement that there could then be no possibility of dropping the work. These polyamides (polymeric amides) could be made from diamines and diacids in this way:



and then two molecules of this condensate would react to give:



and this long molecule would then react with itself, eventually forming a long polymer. Another way in which the polyamides could be made was by starting with a molecule which at one end had an amino-group and at the other end a carboxylic acid group. This could react with itself in this way:



Two molecules of this condensate would then react to produce:



this would react with itself, and so both methods gave very similar polyamides, which were fibre-forming. The first method was chosen for use in preference to the second simply because it was easier and cheaper to make diamines and dicarboxylic acids than it was to make amino-acids.

The result of the research was that strong fibres could be produced

—fibres which were different from any other fibres, in that they were truly synthetic. The long-chain polymeric molecules had been built up in the laboratory by man from short, simple molecules. In no case previously had a fibre been so made. True, artificial fibres such as nitrocellulose, viscose and cellulose acetate had been made, but all these had used the original polymer which Nature had provided in the form of the cellulose molecule in the wood or cotton used as the raw material. Carothers synthesised the polymer—his nylon was the first true synthetic fibre—his achievement was outstanding.

By 1938 the du Pont Company were making nylon at a small pilot plant at Wilmington in U.S.A. Since then other large plants have been built in America. In this country the fibre is spun by I.C.I. Ltd., at Doncaster, at Pontypool, and at Gloucester; and by other manufacturers throughout the world.

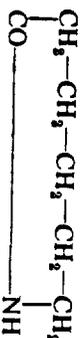
The history of nylon is one of the great romances of science; the success of nylon has exceeded all expectations.

CHEMICAL STRUCTURE

Normal nylon, which is made from adipic acid,



and hexamethylene diamine, $\text{NH}_2(\text{CH}_2)_6\text{NH}_2$, is referred to as "66" nylon because each of the raw materials contains 6 carbon atoms. A similar polyamide can be made from sebacic acid, $\text{COOH}(\text{CH}_2)_8\text{COOH}$, and hexamethylene diamine and by the same reasoning this is known as the "610" polymer. Another polymer known as nylon 6 and made from caprolactam



which reacts as if it were ϵ -amino-caproic acid, $\text{COOH}(\text{CH}_2)_5\text{NH}_2$, has also been made on a very large scale (p. 376).

The "66" type is preferred to the 610 polymer, partly for reasons of superiority of the fibre—it has, for example, a melting point higher than that of the "610" polymer, and also because organic compounds containing 6 carbon atoms in a straight line are conveniently and cheaply derived from benzene or one of its substitution products such as phenol. There is no such cheap raw material for sebacic acid—it can be made from castor oil, which is probably not available in unlimited supply, or it can be synthesised rather deviously from one of the 6 carbon atom compounds. The manufacturing

chemist finds it much cheaper and more convenient to make organic compounds which contain six carbon atoms than any other number.

Stabilisation. It should be noted particularly that the molecules of nylon are long and straight, that there are no side-chains or cross-linkages. Those polymers which are spun as nylon have molecular weight averages of the order of 12,000–20,000. If the molecular weight is below 6,000 it is unlikely that the polymer will form fibres at all; the fibres that are formed with low molecular weight (say 6,000–10,000) are weak and brittle; then, as the degree of polymerisation and the molecular weight increase, the fibres become strong. Correspondingly, the molecular weight must not be allowed to become too high; if it is well over 20,000 the polymer becomes difficult to melt or to dissolve. Therefore, the process of polymerisation must not be allowed to go on indefinitely, but must be stopped at a given molecular weight. This is achieved by a process known as "stabilisation". If, instead of taking exactly equivalent quantities of adipic acid and hexamethylene diamine, an excess of, say, 2 per cent of the former is taken, the time will soon develop when all the long polymeric molecules have carboxylic groups at both ends, instead of a carboxylic group at one end and an amino-group at the other. When this happens, it is impossible for polymerisation to proceed further, and the polymer is "stabilised". Perhaps it is advisable to elaborate this explanation of stabilisation a little. It will be appreciated that if, instead of taking equimolecular quantities of diamine and diacid, one takes 1 equivalent of diamine to 2 of acid, then the reaction will go as far as:



It can go no farther, because all the end-groups are now acidic, and there are no free amino-groups for them to react with. Next, suppose that, instead of using a ratio of 1:2 of diamine to acid, we use one of 1:1.5 or 2:3. Then the reaction is as follows:



This time a longer polymer has resulted, and as the ratio of diamine: diacid approaches unity, the length of polymer formed, before stabilisation prevents longer chain formation, will become greater. A ratio of 1 diamine: 1.02 diacid gives a polymer with a stabilised molecular weight of about 12,000 and one which is suitable for nylon preparation. Stabilisation (this method is used on production) can also be effected by using exactly equimolecular quantities of

diamine and diacid and adding perhaps 1 per cent of a mono-functional reagent such as acetic acid; this has the same effect as the excess of diacid; when the length of molecular chain becomes sufficiently great all the amino-groups are prevented from further participation in polymerisation because they are "protected" by acetyl groups. Accordingly, polymerisation can be stopped at a predetermined stage by using excess of one of the reactants, or by introducing a mono-functional reagent. As a corollary it will be appreciated how important it is that the reacting materials, usually adipic acid and hexamethylene diamine, should be very pure; the presence in them of a small quantity of impurity may be quite sufficient to prevent the polymer growing long enough to give high tenacity fibres. The word "stabilise" is used in two senses in relation to nylon and similar polymers. The first is that of limiting the polymer growth during formation and this is the process that has just been described; the polymer is stabilised at a defined molecular length of chain. The second is quite different and it relates to stabilising the polymer (most often in the form of already-spun yarn) against degradation when exposed to heat; this is discussed particularly on pp. 391 and 895. The two ideas must be kept separate.

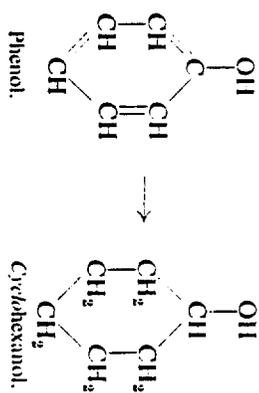
It is sometimes said that nylon is made from coal, air and water; whilst this statement is perhaps a little misleading, it may be justified as follows. Phenol is a coal-tar derivative, the hydrogen necessary for the reduction processes can be obtained from water, and the ammonia from the nitrogen in the air and from hydrogen. All the primary materials necessary for the manufacture of nylon are available in this country. But most of the world's nylon is made from oil.

MANUFACTURE

It is possible to synthesise adipic acid and hexamethylene diamine in more ways than one, but the method which was at first used on production started with phenol. Phenol is made usually by sulphonation of coal tar and benzene, in turn, is made by the distillation of coal tar or alternatively from petroleum.

The phenol is reduced by passing its vapour together with hydrogen gas over a catalyst. Alternatively, it may be reduced in the liquid state in an autoclave, but the vapour-phase method has the advantage that it can be carried out continuously. The product is *cyclohexanol*.

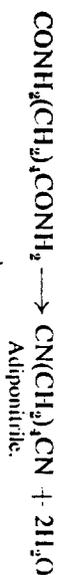
The *cyclohexanol* is oxidised with concentrated nitric acid to adipic acid, the ring being broken. In late 1973 the price of adipic acid in the U.S.A. was 18.5 cents per lb.



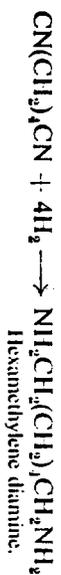
Adipic acid is one of the compounds required for making nylon; the other is hexamethylene diamine, which can be made from adipic acid as follows. The adipic acid is caused to react with ammonia to give the amide:



The amide is dehydrated over a suitable catalyst to give the corresponding nitrile:



The nitrile is reduced with hydrogen in the presence of a cobalt or nickel catalyst in an autoclave:



The hexamethylene diamine and the adipic acid are then dissolved separately in methanol and on mixing the solutions a precipitate of "nylon salt" or hexamethylene diammonium adipate,



is thrown down. The salt may be purified at this stage.

Modern Modification. Nowadays, the usual route for the first stages is no longer benzene \longrightarrow phenol \longrightarrow cyclohexanol but benzene \longrightarrow cyclohexane \longrightarrow cyclohexanol. Air is passed through cyclohexane at 120–150°C. under a pressure of 4 atmospheres to keep the system liquid; cobalt naphthenate is present as a catalyst and the cyclohexane is converted to a mixture of cyclohexanol and

methods. In the end butadiene or some similar 4-carbon compound such as butanediol will probably win.

There is no difficulty nowadays in making chemicals on a large scale; there are usually several possible routes and which one will be used depends on the prices and availability of the raw materials.

Polymerisation. Sufficient stabiliser is added—acetic acid is used for this—and the salt is melted under an atmosphere of nitrogen. Air has to be excluded, or the salt would discolour, and eventually the polymer would char; nitrogen is the most convenient gas to use to provide an inert atmosphere, but hydrogen may be used instead, or, again, a vacuum may be used. It is important only that air is excluded. Water that is split off from the nylon "salt" as polymerisation proceeds is allowed to escape. If melt nylon is required, an aqueous suspension of titanium dioxide is added to the reaction mass during the course of polymerisation; a quantity of 0.3 per cent pigment on the weight of the polymer is sufficient. A temperature of 280° C. and a time of four hours are suitable conditions for polymerisation. It is quite possible to polymerise nylon in another way—*viz.*, in solution in phenol or *m*-cresol—but on the manufacturing scale it is unlikely that any solvent is used. The molten polymer maintained at a temperature of 285–290° C. is extruded through a slot on to a wheel, in ribbon form several inches wide; this ribbon is quenched with cold water as soon as it solidifies, in order to reduce the size of the crystals.

Spinning. Nylon is melt spun. The ribbon of nylon is broken into nylon chips. These are fed through a hopper, *A* (Fig. 118), into a spinning vessel, *B*. In this they fall on to an electrically heated grid, *C*, which has a mesh too small to pass the chips until they have melted. As it melts, the molten nylon passes into the pool *D*; it is desirable to keep this pool small in order to reduce the risk of decomposition and discoloration to which nylon in the molten state is subject. There is therefore a float control on the pool level which controls the electrical heating of the grid—if the pool level rises, the current heating the grid is automatically reduced, and vice versa. In this way the level of the pool of molten nylon may be kept practically constant. A nitrogen atmosphere is maintained over the pool of polymer. The melt (288° C.) is metered by a pump *F* through a filter (not shown) to the orifices *E*. The filter may consist of several layers of metal gauze, the first relatively coarse, the next fine and ultimately very fine, about 300 mesh, and between the gauze layers there may be layers of sand graded in particle size; as the melt passes through the sand, impurities are removed. The orifices are

of about 0.010 in. diameter and are drilled countersunk in a steel plate 0.25 in. thick and about 2 or 3 in. diameter. The melt solidifies immediately it issues from the jets and the so-formed filaments pass through a cooling chamber in which a cold air current *G* is swept across them. If one of the orifices has been too large the filament issuing therefrom will be heavier than the others and will bow more in the airstream than its companions, and if it touches one of them it will fuse to it; it is therefore essential for this reason, as well as for uniformity of denier, to have all the spinning orifices equal in size.

The spinning speed is about 1,200 metres per minute. As the yarn emerges from the cooling chamber it is at a temperature of about 70° C. It is next run through a steam chamber *H*, to wet it before it is wound; if it were wound without this treatment it would later extend a little in length on the package as it picked up moisture from the air to gain equilibrium and would slough off the package. If, however, the yarn is wetted by the steam before winding, this trouble is eliminated. A very slight twist which facilitates subsequent handling may be inserted during spinning.

Melt spinning has two big advantages over solution spinning:

1. It avoids the need for a solvent recovery plant and the losses which always occur during recovery, however well it is done;
2. The high spinning speeds that are possible.

Glass Beads for Filtration. The sand that is used for filtration is quartz sand; it is milled in water so that any grains with sharp edges are rounded, and is then graded for size by screening; it is cleaned free from dust, washed in a 50 per cent solution of nitric acid, is rinsed with distilled water until it gives a neutral reaction and is finally dried. In order to cut out much of this work and in particular the nitric acid treatment, it has been suggested by A. I. Gofman (*Khim. Volokna*, 1969, 69, see also abstract by author in *Tsv. Tekh.*, 12 September 1969) of the Kinskii Combine in Russia, that glass beads should be used as the filtering material instead of quartz sand. The beads are formed at 600° C., and screened, the preferred size being 1–2 mm. They are superior to the sand in that the quality of fibre spun does not deteriorate as spinning continues. Furthermore, they can easily be regenerated for re-use.

Steam Spinning. Some depolymerisation always takes place in the melt and is known to be determined by the amount of water present; in order to reduce it, the polymer flake is dried before it is

used for spinning, but there is always a little moisture present, and as this is variable the degree of depolymerisation that takes place is also variable. A method has been patented (Brit. Pat. 653,757 of 1951) in which a known amount of moisture vapour, usually 0.16 per cent, is added to the nylon in the spinning melt chamber so as to maintain a constant quantity of moisture; some depolymerisation occurs, but the amount that does is controlled and constant. This steam spinning gives a more uniform yarn.

A process has been developed commercially by von Kohorn International Corporation in which the molten pool of polymer waiting to be extruded is maintained under a steam instead of a nitrogen atmosphere. It is said that this reduces the depolymerisation of the nylon with the resultant formation of a little monomer which normally occurs. (This steam spinning process will not be extended to the polyester Terylene, which is too prone to hydrolyse in the melt.)

Cold Drawing. The filaments as they are first spun are not very strong; their tenacity is 1.0-1.3 grams per denier, and they are dull. They are, however, cold drawn by stretching about 400 per cent, giving bright filaments with a tenacity of 5.8 and elongation of 17 per cent. The exact degree of stretch varies with the yarn being spun; fine filaments cannot be drawn down so much as coarse filaments. The reason for this difference is not really established, but is probably bound up with the partial orientation of the molecules on the outer parts of the filaments due to being drawn over the sides of the orifice; the finer the filament, the greater the proportion of "skin" to bulk, and consequently the better is its orientation; if fine filaments are already (before having been cold-drawn) a little better oriented than coarse filaments, then they will not be capable of being cold-drawn so much as the coarse filaments because the stage at which orientation is almost perfect will be reached earlier.

The stretching operation is simple and is illustrated in Fig. 119. Nylon yarn is pulled off the bobbin *L*, which is the primary spinning package; it passes round guides *M*, *N*, between a pair of nip rollers *O*, which determine its initial speed, and goes over a deflector *P* and then two or three times round roller *Q* which has a linear speed about five times that of rollers *O*; then it passes through a guide *R*, and on to a take-up bobbin *S*, twist being inserted as the yarn is taken up. The cold-draw, or degree of stretch, is equal to the ratio of the linear speeds of rollers *Q* and *O*. When a length of undrawn nylon is held one end in each hand and pulled out, the sensation is rather like that of pulling out a telescope; photographs that have

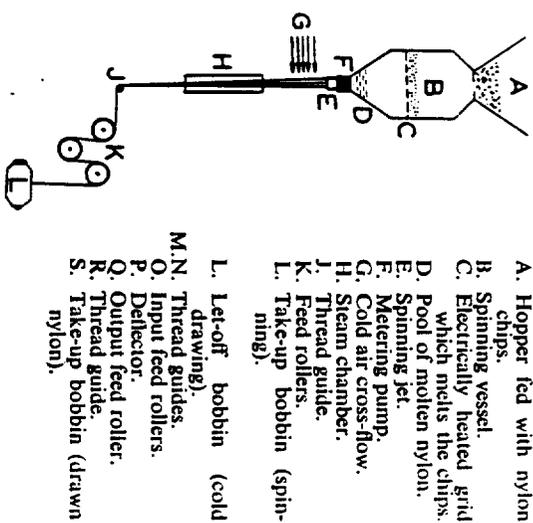


Fig. 118.—Diagrammatic representation of nylon spinning plant.

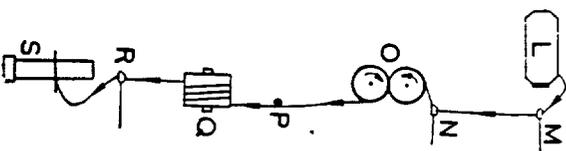


Fig. 119.—Diagrammatic representation of cold drawing of nylon.

been taken during the stretching operation show that the nylon filament necks-down very quickly and not gradually along the free length of the yarn. When the yarn is cold-drawn and the filaments fine down they become lustrous and strong. This is due to the orientation of the molecules. As spun, the molecules are arranged in a random manner and are probably folded, and as they are cold-drawn the folds are removed as shown on p. 100. The final crinkle in the stretched nylon corresponds to the elongation at break. When a filament of nylon has been stretched almost to breaking point, the molecular crinkle has been straightened out. Further stretching causes breakage of the filament. This may be due either to breakage of the molecules or to overcoming the forces (Van der Waals) that hold the molecules together. Breakage of a fibre consists either in breaking the molecules, or in tearing them separate from each other, whichever is easier; the longer the molecules the less likely they are to be torn apart (p. 75).

During the orientation process oil may be applied to the yarn; any high-grade vegetable oil is suitable. The oil is applied simply to facilitate textile processing—it has nothing to do with the orientation.



FIG. 120.—Nylon yarn being tested for denier.

A known length is reeled off the package and weighed. In the illustration, lengths are being reeled off ten packages simultaneously.

Afterwards the yarn is twisted and is ready for use for textile purposes. Fig. 120 shows nylon yarn being tested for denier. In the early days of cellulose acetate spinning, olive oil was the usual lubricant. It oxidised in air and not always uniformly, so that parts of highly oxidised oil were difficult to remove in the dyehouse and caused fabric to be stripy. Then tea-seed oil was used, and this was better, and then triethanolamine oleate, which washed off very easily indeed, was used. But what was simple and straightforward in the early days is not always thought to be so now. One helpful fibres chemist tells me that finish formulation is a delicate art. I am grateful for the knowledge but mildly dismayed. Perhaps he would agree that what oil goes on in the spinning must come off in the dyehouse.

PROPERTIES

Nylon fibres are produced with a range of properties; some which are intended primarily for industrial application have a very high tenacity, others intended for apparel have lower but still high

tenacities; where tenacity is very high, extensibility is lower. Depending on type, the tenacity and elongation at break range from 8.8 grams per denier and 18 per cent to 4.3 grams per denier and 45 per cent. The wet strength is also very high—about 80-90 per cent of the dry strength, a valuable feature. Another most valuable

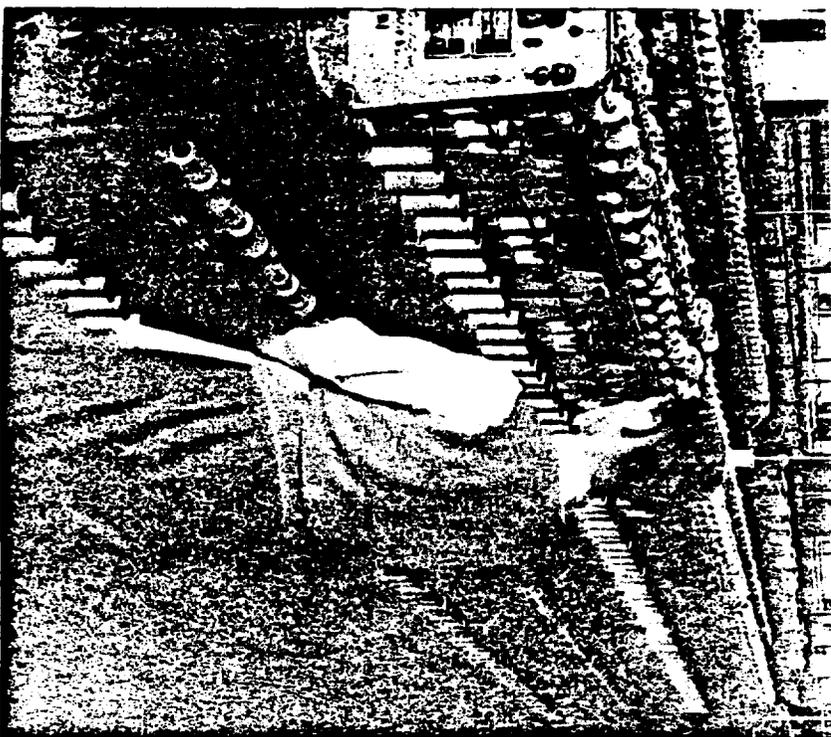


FIG. 121.—Throwing or up-twisting nylon yarn from bobbin to cheese.

feature is that even when knotted the strength of nylon is very high. A half-hitch in a nylon yarn reduces the tenacity by only 15 per cent. Nylon has good flexing qualities and good resistance to abrasion—some four or five times that of wool. A stress-strain diagram for a nylon yarn compared with one for Dacron is shown in Fig. 154 (p. 445).

CHAPTER 20

NYLON 6, NYLON 7, NYLON 11

PERLON, CAPROLAN, KAPRON, ENANT, RILSAN

The linear polymer made from the α,ω -six carbon amino-acid is known as nylon 6. The acid is 6-aminocaproic acid:



and the polymer, nylon 6, is



where n is about 200.

In 1899, the acid was prepared by S. Gabriel and T. A. Maass; they heated it and found that a tenacious hard material resulted. This was a lump of nylon 6, but they were too far ahead of their time and there was nothing to suggest to them that the material might have some practical applications.

Carothers investigated the fibre-forming possibilities of the polymer of amino-caproic acid as early as 1930; he had some difficulty with it and it was not until 1932 that he published a description of fibre-forming nylon 6 polymers. Carothers and du Pont a little later selected nylon 66 (from hexamethylene diamine and adipic acid) as the most promising fibre and nylon 6 was neglected for a while in America. But in Europe work on it was pushed forward and in 1937 Paul Schlack of I.G. Farbenindustrie at Berlin-Lichtenberg polymerised *caprolactam* to obtain a polyamide that was similar in many ways to du Pont's nylon 66. The polymer, nylon 6, was spun into a fibre in several of the I.G. factories and was called Perlon L; all these factories were situated in what is now the Eastern Zone of Germany and after the war they were all dismantled and their technical staffs dispersed. But a few of the people re-assembled at I.G.'s Bobingen factory in Western Germany and by 1948 were again producing Perlon. Because Bobingen has been merged with Farbwerke Hoechst A.G., much of Germany's nylon 6 production is now called Perlon Hoechst. Another large part of it is made by Bayer and is known as Bayer-Perlon. Strictly, the word "Perlon" is the trademark of the nylon 6 fibre produced by members of the Perlon Warenzeichenverband.

Incidentally, it may be noted that during the war small quantities of nylon 66 were made in Germany under the name Perlon T, and

furthermore that a polyurethane fibre (p. 487) was made and called Perlon U. But for a long time, Perlon—the word without a suffix—was used to denote nylon 6. Nowadays it is simply called nylon 6.

All over the world nylon 6 is made: Allied Chemical in America call it Caprolan, in Russia it is called Kapron, in Japan it is called Amilan (Toyo) or often just nylon. These names represent the products of but three of the many, perhaps fifty, manufacturers who make nylon 6.

Growth of Nylon 6

In America du Pont and Chemstrand have concentrated on nylon 66; so have B.N.S. and latterly I.C.I. in Britain. The enormous production of this fibre has overshadowed the world production of nylon 6. Furthermore, whereas nylon 66 melts at about 260°C., nylon 6 melts at about 215–220°C., which puts it at a quite serious disadvantage. Why, then, was nylon 6 manufactured at all? Firstly, those organisations in Germany which had developed the fibre would naturally tend to produce it, rather than switch to du Pont's nylon 66. Secondly, the process for nylon 6 is in some respects simpler than that for nylon 66; Schlack's discovery that nylon 6 could be made simply by heating caprolactam made a big difference because caprolactam can itself be made from cyclohexanone and hydroxylamine which are both easy to make. Thirdly, there has always been a recognition of the superior resistance to light degradation of nylon 6. Fourthly, there has been a growing appreciation that its lower melting point may not make nylon 6 less suitable than nylon 66 for tyre cords; there is no likelihood of the temperature of a tyre exceeding 130°C. in use, and at temperatures such as this the resistance of nylon 6 to degradation is actually superior to that of nylon 66. Even in America, birthplace of nylon 66 (and indeed of all nylon), nylon 6 is advancing; at the end of 1961 five manufacturers there were making a total of about 50 million lb. a year, about 12 per cent of the U.S. production of nylon 66. Yet the fibre was not made in the U.S.A. at all before 1954.

A new factor which may push nylon 6 in future to the disadvantage of nylon 66 is the discovery by Sniia Viscosi of a new and cheaper method of making caprolactam from toluene; this process has already been licensed to some spinners.

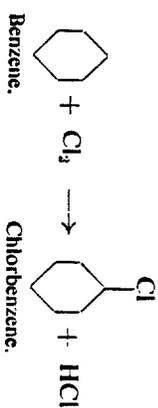
Nylon 6 has demonstrable advantages over nylon 66 in respect of dyeability, elastic recovery, fatigue resistance and thermal stability. In the U.K. British Enkalon now produce it in Northern Ireland, Courtaulds make it under the name Celon at Aintree and Spondon. It was at one time reported that I.C.I. were to use a Soviet process

for their caprolactam but it appears now that both the Soviet Union and I.C.I. are to use a Swiss (Emser Werke/Inventa) process. In the event (1972), I.C.I. have never produced nylon 6 commercially.

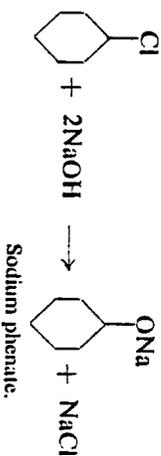
Manufacture

The reactions by which nylon 6 has been made are as follows:

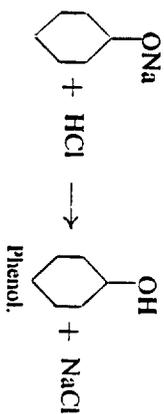
From Benzene through Phenol. Coal is the raw material, tar is obtained from it and on distillation one of the fractions obtained is benzene. The benzene is chlorinated to give monochlorobenzene:



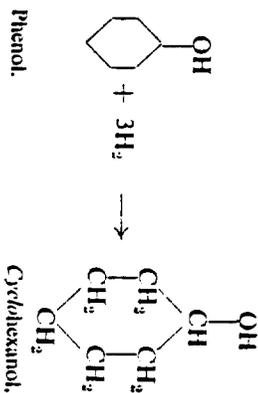
The chlorobenzene is treated with caustic soda to yield sodium phenate:



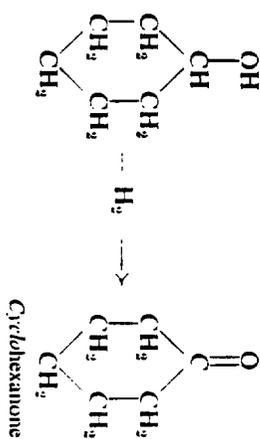
and on acidification, phenol results



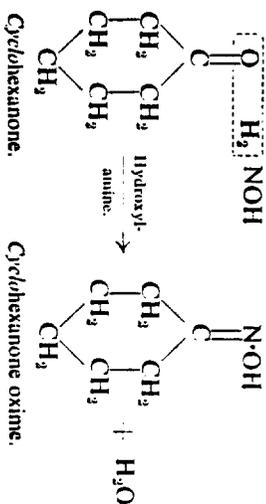
The phenol is reduced with hydrogen under pressure in an autoclave using nickel as a catalyst to give *cyclohexanol*



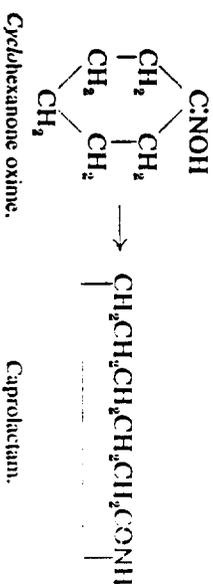
The *cyclohexanol* is purified by distillation and then partially dehydrogenated using copper as a catalyst to the ketone *cyclohexanone*



Hydroxylamine which is produced from ammoniacal liquor, also derived from the coal tar, is then reacted with the *cyclohexanone* to yield *cyclohexanone oxime*. The hydroxylamine is used as the sulphate ($\text{NH}_2\text{OH}\cdot\text{H}_2\text{SO}_4$) in aqueous solution at 20° C. As it reacts with the *cyclohexanone*, sulphuric acid is liberated and ammonia is passed in to neutralise the acid, the temperature rising to 90° C. After settling, the organic phase is crude *cyclohexanone oxime*.



The oxime is then caused to undergo the Beckmann transformation by treatment with sulphuric acid which converts it into caprolactam:



wise some tarry material, which is useless and wasteful, is produced. Light of this wavelength is ultra-violet; nothing of wavelength shorter than 3,930 Å (violet) is visible. The Toray process is known as the PNC (short for photomicrosation of *cyclohexane*) process.

Such a simple chemical as caprolactam can be synthesised in many ways. It may be doubted if the phenol-based route is still used and if the Snia Viscosa process ever was. Perhaps the Toray PNC is the most important process industrially. Manufacturers do not readily disclose their important processes. So many are protected by patents that the two or three industrially important methods may be hidden under a welter of possible or problematical processes.

Polymerisation. Two alternative methods are used:

1. The lactam is liquefied, filtered and heated in an autoclave under high pressure and about 200 of the small monomeric molecules unite to give one large polymeric molecule of Perlon $\text{H}[\text{—NH—}(\text{CH}_2)_6\text{CO—}]_{200}\text{OH}$. Although the number 200 is assigned to this molecule this at the best represents a number average and actually the polymer will consist of molecules of different lengths. The polymer, Perlon, is known as "nylon 6" because each repeating unit contains six carbon atoms.

2. The lactam has 10 per cent of its weight of water added, and the polymerisation is carried out at a high temperature with a controlled escape of steam. This process takes longer than the first but is easier to control in that there is less chance of locally overheating and so spoiling the molten material during the early stages of polymerisation. The caprolactam, it will be noted, behaves on being heated as if it were ϵ -aminocaproic acid and this is the fundamental basis of the process.

Whichever method of polymerisation is used, some unchanged monomer remains and this is washed out with water in an extractor, otherwise it would weaken and spoil the final fibre.

Spinning. The washed and dried polymer is melted to a clear liquid. It is one of the advantages of nylon 6 that because its melting point is lower than that of nylon 66 it can be melt-spun at a lower temperature. It is metered through pumps to the spinning orifices and is spun straight into atmosphere; the spinning speed can be as high as 1,000 metres/min. The polymer freezes at once in the cold of the atmosphere and the fibres which result from the freezing are passed round two rollers; the first applies water and a wetting agent and the second an oil-water emulsion. This conditions the yarn.

The method used for nylon 66 of passing the yarn as it is spun through a steam chamber is not suitable for Perlon (nylon 6) because

there is such a relatively high concentration of monomer in the Perlon that the filaments of the yarn would become sticky if steamed and liable to adhere either to the walls of the vessel or to each other. Next, the yarn is stretched to about five times its original length to orient the constituent linear molecules and thereby to make the filaments strong, supple and unshrinkable (*i.e.*, the stretch is reversible). The yarn is washed again with water to remove any low polymer, dried and cone wound. If staple fibre is required instead of continuous filament, then instead of being cone wound the yarn is crimped, cut and baled. A part of the process—from the molten lactam to the staple—is shown in Fig. 137.

Continuous polymerisation processes have been developed in recent years: molten caprolactam containing titanium dioxide delustrant and some acetic acid as stabiliser is passed through tubes about 50–100 feet long heated at 260°C. and the polymer that emerges continuously is ready to be spun. The practical difficulty is to secure uniformity of heating; the advantages are higher and cheaper production.

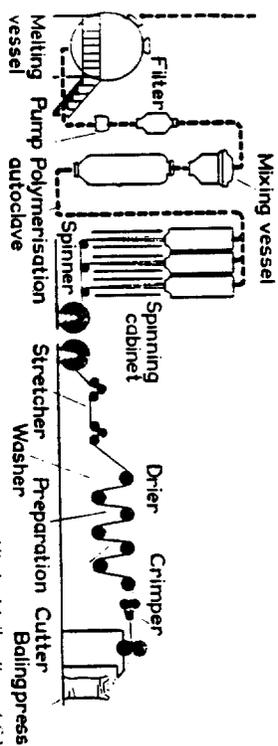


Fig. 137.—Perlon manufacture from molten lactam to staple fibre.

Vickers-Zimmer Process. This is the Consumer-Synthesist Process, the do-it-yourself job, but it must be remembered that Vickers-Zimmer is now Zimmer A.G. (*cf.* p. 71). There is a variety of processes available for nylon 6. If the spun yarn is to be used for industrial or technical purposes, such as tyre cord or carpet yarn, then the process can be shortened by feeding the polymer straight to spinning without intermediate formation and isolation of "chip". As an example, the process for the production of nylon 6 carpet yarn consists of the following stages:

- (a) Solid caprolactam in the form of powder or flakes is melted in the melter, 1 (Fig. 138).
- (b) The molten caprolactam is fed batchwise into the mixer, 2, where the catalyst and the stabiliser are mixed in.

(c) The mix is drained through a filter into an intermediate vessel, 3, to a dosing and mixing system, 4, where the delustrant, normally titanium dioxide, is added.

(d) In vessel 5 polymerisation takes place continuously under pressure, the polymer being raw nylon, 6.

(e) The polymer passes to vessel 6, where polymerisation is continued, but under atmospheric pressure. This is an equalisation stage and improves the uniformity of the product.

(f) The molten polymer is transferred continuously to the vacuum stage in vessels 7 and 8 to remove by distillation any incompletely polymerised and consequently low-molecular-weight polymer.

(g) The melt from the vacuum stage enters the spinning plant through a distribution system, 9, and is spun directly.

The elimination of the chip isolation cuts down the cost of running the process. The capital cost for a plant including buildings which

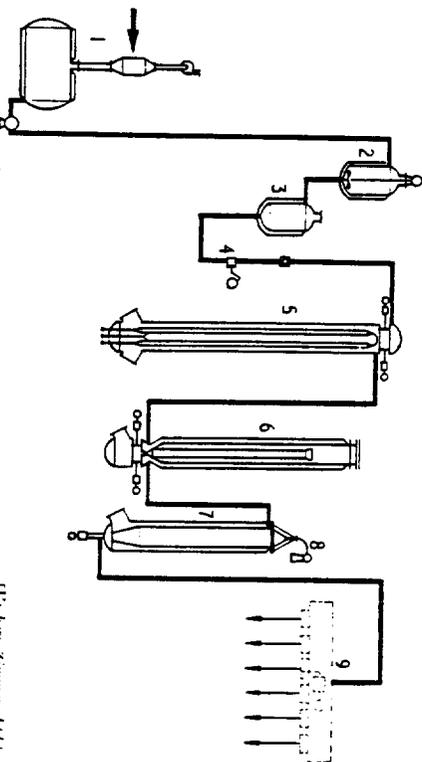


FIG. 138.—Vickers-Zimmer plant flow sheet for conversion of caprolactam into unpurified spinning melt. [Vickers-Zimmer, Ltd.]

working continuously could produce 4.75 million lb. of carpet yarn per year, *i.e.*, roughly six tons a day, would be £1.6 million. The cost of producing the yarn would be somewhat as follows:

	(d./lb.)
Depreciation	8.0
Maintenance	8.0
Personnel	7.6
Raw materials	31.9
Power, oil, water, nitrogen, hydrogen	5.5
	61.0

The biggest single item is naturally the caprolactam, which accounts for more than 97 per cent of the raw material costs: it is costed at 30.5d./lb. Its polymerisation and conversion into carpet yarn costs as much again, so that the final cost is 61d./lb. The personnel item (7.6d./lb. of product) includes labour for the production of yarn only, and does not include labour for any textile processes that may follow the spinning operation. It would be difficult to bring this costing up to date. Vickers-Zimmer has gone, the penny (d) has gone and there has been a glut of fibre from which we are only just recovering. It seems better to leave the old costing to show what the position was in 1969. Contemporary prices (not costs) are shown in Chapter 51.

The specification that the caprolactam which is used for the synthesis should meet is:

Melting point	68.5°C.
Permanganate number	More than 950
Volatiles	Less than 1 c.c. N/10 HCl per 20 gm. lactam

Moisture	Less than 0.15 per cent
Iron content	Less than 10 p.p.m.

The specification that the product, the polycaprolactam or nylon 6, should meet is:

Relative viscosity	2.5–3.2
Moisture	Less than 0.07 per cent
Extractables	Less than 3 per cent

The process described above consists essentially of continuous polymerisation at elevated pressure, of vacuum treatment to remove impurities and of direct spinning.

Vickers-Zimmer Process with Chip Isolation. But if the yarn to be spun is intended for some demanding end-use, such as continuous filament for textile processing, then it will be preferable to use a modified process, one in which the polymer is isolated immediately as chip which can be extracted to remove unchanged monomer and oligomers, *i.e.*, low polymers consisting of only a few molecules of monomer strung together and still sufficiently soluble to be extractable. The chip can thus not only be thoroughly purified but can also be completely dried. Essentially, this whole process consists of the continuous polymerisation of caprolactam at atmospheric pressure, chip production, extraction and drying to provide a product suitable for spinning. The stages in the process are:

- (a) Solid caprolactam powder or flakes is melted in the melter, 1 (Fig. 139).
 (b) The melt is fed batchwise to the mixer, 2, where catalyst and stabiliser are mixed in.
 (c) The mix is drained through a filter into an intermediate vessel, 3, to a dosing and mixing system, 4, where delustrant is added.

(N.B. So far the process is just the same as in that described above, but now comes a difference.)

(d) The lactam is passed continuously to reactor 5, where it polymerises continuously at *atmospheric* pressure under a blanket of nitrogen to nylon 6. The polymerisation is stimulated by heat and by the presence of the catalyst which was mixed in earlier.

(e) The melt is pumped to a chip-spinning head, 6, and is pumped through jets, from which it emerges like spaghetti. The "spaghetti" is cooled in a cooling vat, 7, and is then cut to chip of uniform length in a cutter, 8.

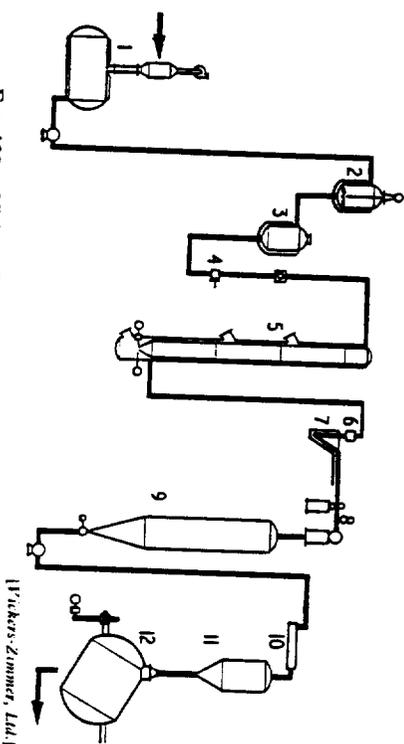


FIG. 139.—Vickers-Zimmer plant flow sheet for conversion of caprolactam into purified chip polymer.

(f) The chip falls into an extractor, 9, where any unchanged monomer and oligomers are washed out with demineralised water.

(g) The washed chip passes through a separator, 10, into a drip pan, 11, and is dried under vacuum in the tilted drum drier, 12. It is then ready for spinning.

The specification for the raw material, the caprolactam, should be

the same as adduced earlier (p. 385). The product, the polymer, should have these properties:

Relative viscosity	2.2-2.6
Moisture	Less than 0.08 per cent
Extractables	Less than 0.7 per cent
Chip dimensions	Diameter, 1.5-3 mm. Length, 2-4 mm.

It will be appreciated that isolation of the polymer in the solid chip form at an intermediate stage increases the cost of the process, compared with that described earlier.

Spinning Machine

In Fig. 140 there is shown a modern spinning machine for nylon 6, one that is made by Zimmer A.G. and is recommended (*E.C.N. Synthetic Fibres Supplement*, 29 October 1971) by them for spinning nylon 6 for tyre cord. It is interesting to compare it with Fig. 118 which shows a spinning machine for nylon 66 and which is at least ten years old. Not much change has taken place, and indeed if comparison were made with a spinning machine 30 years old, the two could be much the same in important matters. The new machine will run faster, up to 600 m./min. and it will give stronger yarn. Special attention is drawn to the after-heaters which are situated just below the spinnerets. They prevent the polymer solidifying too quickly; a relatively slow fibre formation is often helpful (*cf.* slow precipitation of polyinosic filaments, p. 280) in producing extra good properties. The properties of the basic yarn made on Zimmer's machine are:

Tenacity	9.2-9.6 gm/denier
Elongation at break	15-18 per cent
Per cent shrinkage on boiling	12-15

When this basic yarn has been converted into cord, this has a tenacity of 7.6-7.8 gm./denier and an elongation at break of 26-28 per cent. A point to note is the lubrication of the yarn. It is essential in spinning any yarn to give it a finish, to oil it; if this is not done the filaments that make up the yarn will electricify and balloon out; in this state they are easily damaged and some will be broken and the yarn will be hairy. In the Zimmer machine the thread is given a suitable finish just after it has passed through the spinning duct; various components are used in the finish that is applied.

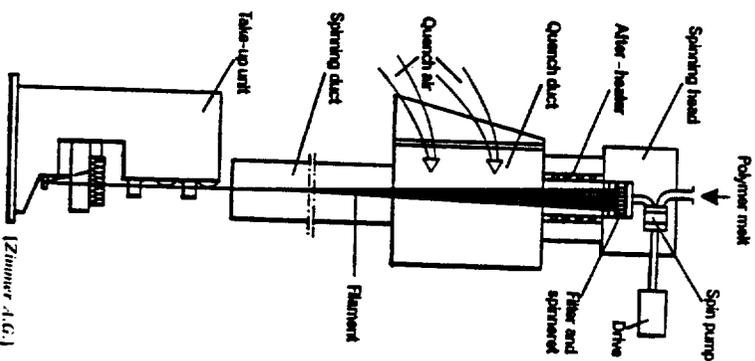


Fig. 140.—Schematic representation of a nylon 6 spinning unit with after-heater. The polymer is fed in at the top; the yarn is taken off at the bottom.

It is of interest to note what Zimmer's consider are necessary properties of the basic yarn for tyre cord; they are:

1. High fatigue resistance.
2. High tenacity.
3. The polymer from which it is made must be as homogeneous as possible and contain neither gel particles nor contamination.
4. A much higher degree of polymerisation is necessary in the polymer if it is to meet conditions 1 and 2, than is used in apparel nylon. The high D.P. with its higher than usual melt viscosity means that measures must be taken to mix and blend the molten polymer. In the main, this is done by a screw feed.
5. The Young's modulus (p. 651), which is inevitably lower in nylon 6 than in rayon and polyester, should be as high as possible.

The one real essential is a very high degree of polymerisation; almost all follows from that. The D.P. for tyre cord must be much higher than for apparel.

Properties

The main difference between this polymer (nylon 6) and nylon 66 is that it has a much lower melting point; this is a serious disadvantage, as any garments made from it must be ironed with considerable care. Stockings, of course, do not need ironing, and for some other garments Bayer's have put the question "to iron or not". The truth of the matter is that all woven goods are much better for a light ironing, and most knitted goods, except hose, are so too, and that although some people maintain that ironing is not necessary with some of the synthetic fibres, its omission leaves some crumpling, even if it is only very light, and a lack of smartness.

What has Perlon got to offset this quite serious disadvantage of low melting point? There are two things that merit consideration:

1. The synthesis of caprolactam is easier than that of hexamethylene diamine used in nylon 66; in particular the high pressure catalytic reduction of nitrile to diamine is avoided; probably it is cheaper to make Perlon than nylon 66.
2. The affinity of Perlon for acid dyestuffs seems to be greater than that of nylon 66, due to the greater number of amino end-groups in Perlon than in nylon molecules; the more amino groups there are, the better the affinity of the fibre for acid dyestuffs.

Strength and Extensibility. The strength of nylon 6 can be varied at will up to about 8 grams per denier. Such very high strength is characteristic of yarn for industrial use, with an elongation at break of 16–20 per cent. In yarn for apparel uses where softness of handle is important, representative figures are 5 grams per denier tenacity and 30 per cent elongation. The industrial yarns have been subjected to greater stretch in the drawing process than the apparel yarns.

Specific Gravity. The fibre is light with a specific gravity of 1.14 (wool is 1.31, nylon is 1.14, most of the acrylics are 1.14–1.19).

Moisture Regain. Moisture regain is about 4 per cent, very similar to that of nylon and because nylon with its relatively high moisture regain is probably the best yet of the synthetic fibres for purposes of apparel, Perlon, too, stands high in the list in this respect.

Swelling. Swelling is low; if Perlon is steeped in water and then

CHAPTER 24

POLYESTERS

TERYLENE, DACRON, KODEL, VYCRON

TERYLENE is a synthetic linear polymeric fibre which was invented and developed in this country by chemists (J. R. Whinfield and J. T. Dickson) of the Calico Printers' Association. It is a direct development of the work carried out by W. H. Carothers on polyesters. Whereas Carothers found that the polyamides were more suitable than the polyesters for making fibres, the C.P.A. have made new polyesters with improved properties. A plant for the manufacture of Terylene is operated by I.C.I. at Wilton, Yorks. The du Pont Company in America purchased Whinfield and Dickson's U.S. patent application from C.P.A. Ltd., and received the subsequently issued U.S. Pat. 2,465,319. The polymer has been made and the fibre spun from it in a plant at Kinston, North Carolina, to it in America is "Dacron". Terylene and Dacron has been given chemically; the fibre and yarn made in the U.K. are called Terylene, those made in the U.S.A. are called Dacron. Since those early days it has done well and is now made throughout the world. The same chemical fibre: poly(ethylene terephthalate) is also produced in the U.K. by Hoechst (Trevira), British Enkaton (Terlenka), and Courtaulds (Lirelle). I.C.I. make it not only at Wilton but also at Kilroot in Northern Ireland. In the U.S.A. du Pont's Dacron is best known, and Fiber Industries make polyester under the name Fortrel. But nowadays (1973) polyester is made almost everywhere and is sold under a variety of names. With the exception of some of Japan alone, polyester is made by Kuraray, Asahi, Nippon, Teijin, Toray, Toyobo and Kanegafuchi. Courtauld's Lirelle came into production at Carrickfergus in 1971.

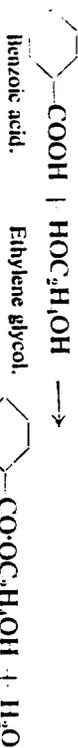
Chemical Nature

Terylene is a polymeric ester; an ester is formed by reacting an acid with an alcohol, in the case of Terylene the acid is terephthalic acid and the alcohol is ethylene glycol. It will be seen that both acid and alcohol are bifunctional, the acid containing two $-COOH$

or carboxylic acid groups and the glycol two hydroxyl groups. If the acid and alcohol contained only one functional group, the reaction would stop at the monomeric stage, thus:



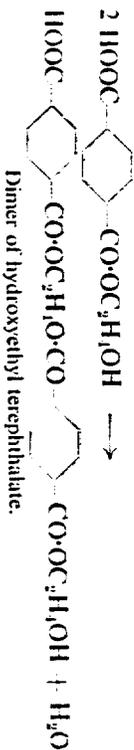
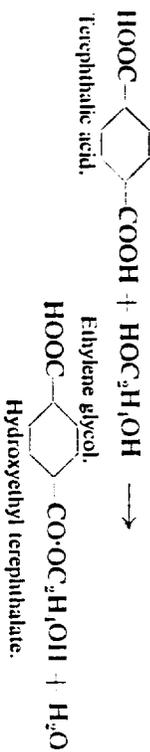
The ethyl benzoate has no sufficiently reactive end-groups and the reaction cannot go further. Even if one of the components, say the alcohol, was bifunctional but not the other, still only a simple monomeric ester can be formed, thus:



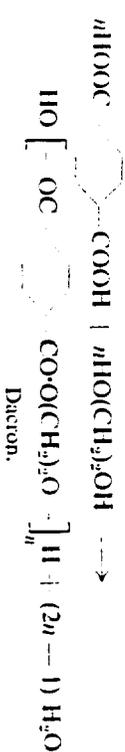
A little ethylene dibenzoate



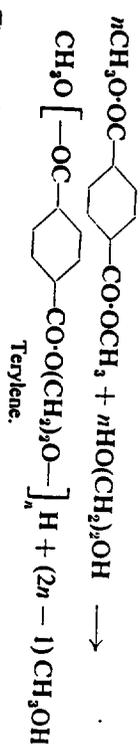
would also be formed. But if *both* the acid and the alcohol are bifunctional then the reaction can proceed indefinitely to form a polymer, thus:



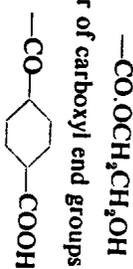
The product, the dimer, still contains reactive groups at either end of its molecule, so that polymerisation can proceed, and a high polymer, containing, say, eighty benzene nuclei, will eventually be formed and will yield good fibres. The American fibre Dacron is made as just outlined from the acid, and the complete reaction can be written:



The British fibre Terylene is made by polymerising the dimethyl ester of terephthalic acid with ethylene glycol, and the complete reaction can be expressed:



The product is essentially the same as Dacron. In either fibre the end groups are mainly hydroxyethyl ester:

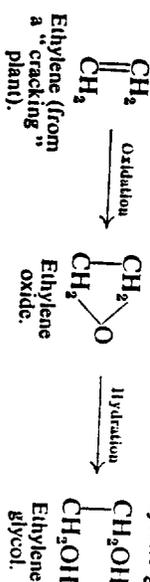


with a small number of carboxyl end groups:

Probably the use of the ester instead of the acid is preferred as purity of reactants is essential, and it is easier to purify dimethyl terephthalate than terephthalic acid itself by distillation at a fairly low temperature. But methods of making pure terephthalic acid have been greatly improved and by late 1972 there was probably more terephthalic acid than dimethyl terephthalate used in the manufacture of polyester.

Manufacture

The schematic flowsheet for the manufacture of Terylene is shown in Fig. 152. The raw material for British Terylene is oil which comes from the Middle East, and from which *p*-xylene and ethylene glycol are made at Wilton. In America the raw material is American oil. The oil is cracked to give ethylene, which is catalytically oxidised with air to ethylene oxide, which is hydrated to ethylene glycol.



Terephthalic acid is made from *para*-xylene, which must be free from the *ortho* and *meta* isomers. The *p*-xylene comes from the C_8 fraction of the naphtha that is distilled from the petroleum. At one time it could not be separated from the *ortho* and *meta* isomers by distillation, because the boiling points of all three are very close together; it was in practice separated by crystallisation: *p*-xylene

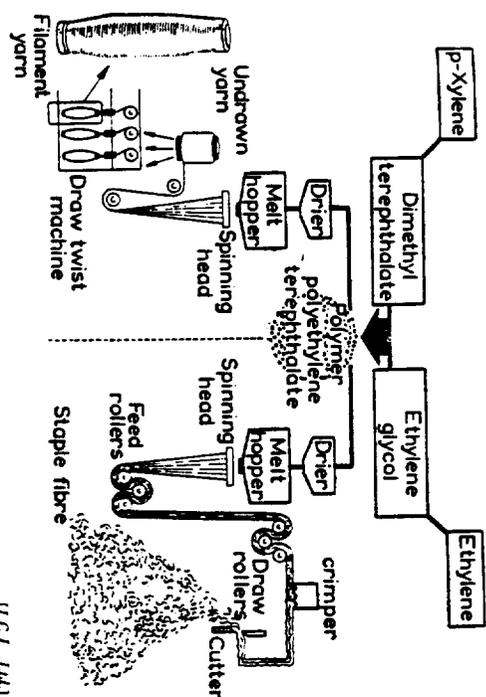
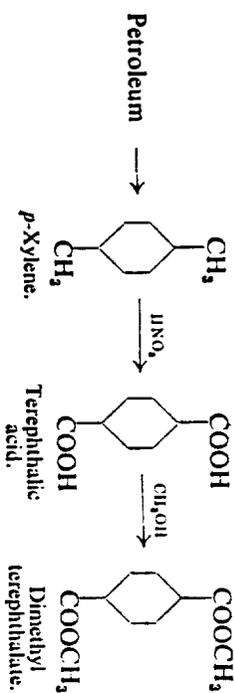


FIG. 152.—Flowsheet for manufacture of Terylene.

(I.C.I., Ltd.)

freezes at 13°C , *m*-xylene at -48°C and *o*-xylene at -25°C . Nitric acid oxidation of the *p*-xylene is used by du Pont; at a temperature of 220°C and 30 atmospheres pressure to maintain liquid conditions, the yield is 80–90 per cent of terephthalic acid. An alternative which is probably used in the U.K. is to oxidise the *p*-xylene with air at 200°C using cobalt toluate as a catalyst, first to toluic acid which is esterified to methyl toluate and this on further oxidation gives monomethyl terephthalate. This or the terephthalic acid from the nitric acid process is converted into dimethyl terephthalate. Either terephthalic acid or its ester can be used to synthesise Terylene or Dacron. The reactions involved in the first of these two processes are:



The terephthalic ester and ethylene glycol are polymerised *in vacuo* at a high temperature. There are two stages in the preparation of the fibre-forming polymer:

1. Ester interchange which is carried out at or near to atmospheric pressure, starting at a temperature just above the melting point of dimethyl terephthalate and ending at a temperature above 200° C., the boiling point of the mixture of excess glycol and polyester low polymers (oligomers) produced. All this time methanol is evolved and condensed for recovery. A suitable catalyst to help this stage along is about 0.05 per cent of a cobalt salt.

2. The polycondensation in which the low polymers made in (1) condense together to build up to long polymeric chains. This stage is carried out at 270° C. (or a little higher), to keep the mass molten, and pressure is reduced to 0.5 torr to assist in the removal of glycol. Catalysts that are used to help this second stage along are a phosphate and a compound of antimony or of germanium.

The polymer is extruded in the form of a ribbon from the autoclave (pressure vessel in which the polymerisation took place) on to a casting wheel. The ribbon of polymer solidifies on the wheel and is then cut into chips (little cubes of about 4 mm. sides) for easy handling, and these are conveyed by suction to the spinning building. The polymer chips are dried to remove residual moisture and are then put into hopper reservoirs ready for melting. The fibre is spun from the molten polymer—a very advantageous feature—through a spinneret with circular holes; the individual filaments solidify almost instantaneously and are drawn together and wound on to cylinders as undrawn yarn at a speed of 1,000 m./min. or higher. This yarn is taken to draw-twist machines, where it is hot-stretched to about five times its original length and correspondingly to about one-fifth of its original denier. This yarn is then supplied to customers, who often re-twist it before use, and set or stabilise the twist by heating it in an oven. Two kinds of Terylene filament yarn are made, (a) yarns of normal strength, which are used mainly for clothing, (b) high-tenacity yarn for industrial uses; the higher tenacity of the latter is accompanied by a lower extensibility, and these changes are brought about by "drawing" or stretching to a greater extent than in the normal yarn. Very coarse filament yarns, owing to their poor thermal conductivity, have to be drawn or stretched cold instead of hot; fine filament yarns are always hot-stretched; the undrawn yarn can be stretched or drawn cold, but less easily and less uniformly than when hot. Accordingly, except for very coarse filament yarns, the drawing process is carried out hot.

Staple Fibre Production. Staple fibre is made in just the same way until the spinning operation; a great number (very many times more than when filament yarn is being spun) of filaments are spun and are brought together to form a thick tow. This tow is drawn, crimped mechanically to reproduce in part the crimp of wool, and the crimp is set or stabilised by heating; the tow is cut into specified lengths of a few inches according to the textile process for which it is intended and is baled. It is made in deniers and staple lengths suitable for spinning on the worsted, woollen, cotton and flax systems. Normal yarn is produced both bright and dull, the reduction of lustre being achieved in the usual way by the inclusion of a little titanium dioxide pigment, but the high-tenacity yarn, for industrial use, is produced only bright.

The flowsheet for the manufacture of continuous filament and staple fibre Terylene is shown in Fig. 152.

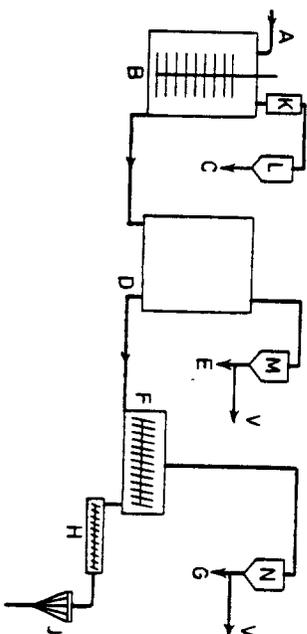
Moisture. One point to which attention should be drawn is that, because polyester is so readily hydrolysed, it is essential to dry the solid polymer before melt spinning is started. This is avoided where molten polymer is fed directly from a continuous polymeriser (p. 440) to the spinning heads. But in other cases where the solid polymer is isolated, as it is in batch methods, it is dried in rotary driers at about 120° C. The final moisture content just before spinning should not exceed 1 part water in 20,000 parts polymer.

Pigmentation. A great deal of polyester has a dulled lustre which is achieved by the incorporation of tiny particles of titanium dioxide in the fibre. The particles have to be very small, otherwise they would block up the spinning orifices, the jets. A widely used method is to mill, *i.e.*, to grind very finely, the titanium dioxide in ethylene glycol and then to add the resulting dispersion to the polymerisation vessel; this gives the uniformity of dispersion which is necessary. The amount of pigment added may be as high as 3 per cent on the weight of fibre in very dull yarns, but is more usually about 0.3 to 0.5 per cent on apparel fibres. Black (carbon black) pigment can be incorporated in the same way, and even some colours, although not many dyestuffs are sufficiently stable to heat to withstand the spinning temperature. The same fibre is produced in Canada under the name Terylene and under licence in Germany, where it is called Dieren and Trevira, in Italy (Terital), in France (Tergal), in Holland (Terleka) and in Japan (Tetoron). By now the patents have run out and with them the licences. A free-for-all prevails. World production of polyester fibre in 1970 was about 3,600 million lb. per annum, of which 2,200 was staple and 1,400 million lb. was filament.

Continuous Polymerisation

All of the large producers now use a continuous polymerisation process; it is cheaper and needs less labour than batch processes do. When once these continuous processes are running they look simple enough, and give a good consistent product, but to begin with it is quite a tricky operation to feed terephthalic acid and glycol in at one end of a plant and take out polyester of determined characteristics and in particular of a known viscosity at the other end. The difficulties should not be minimised; continuous polymerisation is quite an achievement. Sometimes the plant designers and the process staff and operatives who have to work the plant, go even further and run their viscous polyester straight to a spinning machine.

A diagrammatic arrangement of a continuous polymerisation and spinning plant for polyester is shown in Fig. 153. Terephthalic acid



(after J. E. McIntyre)

Fig. 153.—Equipment for continuous polymerisation to yield polyester.

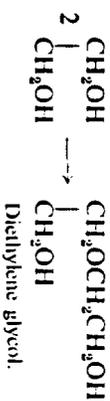
- A. Feed of ethylene glycol and terephthalic acid.
- B. Esterifying vessel (at 2800 torr or 2800 mm Hg).
- C. Condensed water collector.
- D. Pre-polymerising vessel.
- E. Condensed water and glycol collector.
- F. Polymerising vessel.
- G. Condensed glycol collector.
- H. Extruder.
- J. Spinning head.
- K. Fractionating column.
- L, M, N. Condensers.

(or dimethyl terephthalate) and ethylene glycol are fed at *A* into the esterifying vessel *B* which is fitted with a stirrer and is maintained at a temperature of 235–250° C. and a pressure of about 2,800 torr; the carboxyl groups of the acid catalyse the reaction, no added catalyst is necessary. Water is given off at point *C*, this coming from the reaction of acid and glycol. The low polymer is transferred

continuously to a pre-polymeriser *D* which is maintained at 220–275° C.; a catalyst is used, sometimes an oxide or salt of manganese or cobalt present in a concentration of 0.01–0.1 moles per hundred moles of polymer. Poly-condensation takes place, and water and ethylene glycol are eliminated and collected at point *E*; the viscosity has risen and a driven screw or some such device is necessary to move the polymer into the next vessel *F*—a polymeriser which is maintained at 280–290° C.; the temperature has to be high because the polymer now has a higher melting point and the melt is very viscous indeed, so that it is difficult to work. Raising the temperature reduces the viscosity and mitigates this trouble. As polymerisation proceeds, a vacuum is applied to facilitate removal of the glycol which is given off and collected at *G*; the pressure is reduced to about 0.5 torr. In this final polymerisation stage a different catalyst, usually a germanium or pentavalent antimony compound, is added.

The apparatus shown in Fig. 153 consists of three reactor vessels, but more are sometimes used, largely depending on the final degree of polymerisation required; for example, industrial yarns are made from higher molecular weight (and higher viscosity) polyester than are apparel fibres. Finally, an extruder *H*, usually of a screw type, pushes out the polymer to be cast and made into chips for later spinning. But in the more sophisticated plants the molten high viscosity polymer may be fed directly to spinning units *J* (called spinning heads), as shown in Fig. 153. The monomeric constituents are fed in at *A*, polyester fibre comes out at *J*. Twenty years ago it would have been miraculous; today it is commonplace.

Impurities. There are two impurities normally present in polyester fibres. A small part of the ethylene glycol used in the synthesis is itself converted to diethylene glycol,

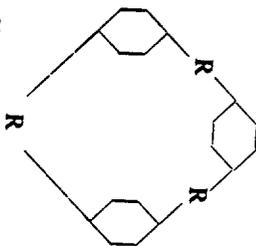


and from this there occur in the polyester a few (1–3 mole per cent) groups such as:



which contain an ether linkage.

The other impurity normally present to the extent of 1.5 per cent in the polymer, and in the fibre derived from it, is the cyclic trimer (R—COOC₂H₄OOC—)



It may wash out of the fibre during fabric dyeing, float on the dyebath and re-precipitate on the dyed fabric; it is undesirable. These two impurities occur in polyester irrespective of whether it has been made by a batch or a continuous process of polymerisation.

Solid State Polymerisation

This process is in its infancy; some people think that it may develop into one of importance. It seems to have been born out of a desire to obviate the difficulty of heat transfer and uniformity of polymerisation through a highly viscous mass. The solid low polymer has to be made first and converted into small particles of about 100 mesh before it is subjected in solid particle form to a temperature of 220–240° (below the melting point). The particles may be fluidised in an inert gas stream or agitated under reduced pressure to prevent sintering. Polymerisation goes rapidly because glycol (from the low molecular weight polymer) diffuses rapidly to the particle surface.

Vickers-Zimmer Process. If a consumer uses two tons a day or 1.7 million lb. a year of polyester it may be worth his while to make his own. Vickers-Zimmer supply the plant, get it going and leave technical staff working on it until it is running smoothly. The cost of installing a plant is not so colossal as might be thought. For example, a plant capable of making 18 tons a day (14 million lb. a year) of polyester staple fibre would cost not much more than £3 million including buildings. Production of staple fibre would cost around 34–36d./lb., made up as follows:

	Pence per lb. of fibre.
Amortisation (10 per cent of plant cost per year)	5.4
Maintenance	0.9
Personnel	3.4
Raw materials	22.7
Power, steam, water, nitrogen, etc.	3.4
Research and development	4.9
	<hr/> 36.7
Less value of recovered glycol and methanol	<hr/> 2.4
	<hr/> <hr/> 34.3

In this costing the biggest item is that of the raw materials. The price of dimethyl terephthalate is taken as 14.5d./lb. and that of ethylene glycol as 7.3d./lb. For the reasons set out on p. 385, no attempt will be made to bring this costing for polyester up to date. Let it stand to show how costs lay in 1969. But *cf.* p. 1021. This plant does not provide for intermediate isolation of polymer chip; the polyester is fed directly from the chemical plant to the spinning machine. The process is continuous; it represents an advance over the batch process, and the various stages that are carried out continuously are as follows:

- (1) Dimethyl terephthalate is fed into a hopper.
- (2) It passes continuously to a melter.
- (3) Ethylene glycol is fed into a storage tank.
- (4) The products from (2) and (3) are run through a dosing system into a reaction vessel where ester interchange takes place.
- (5) The mix from (4) is fed into a stirring vessel at high temperature and reduced pressure, and thence into reactors at high temperature under vacuum where the condensation is completed.
- (6) The product in the melt form is continuously discharged into the spinning machine.

Plants are made in various other sizes, yielding from 1,400 to 29,000 lb. per day of spinnable melt. In other designs the polyester is isolated as chip (about 3.5 mm. long by 2.5 mm. diameter) before being spun.

Properties

The early polyesters that Carothers had made suffered, as fibre-forming materials, from two defects: (1) they were too readily hydrolysed and lacked the chemical stability characteristic of nylon, (2) their melting points were so low that ironing troubles would inevitably have resulted when fabrics made from them were laundered. The discoverers of Terylene have shown that the inclusion of an aromatic (benzene) nucleus in the chain increases the chemical stability and raises the melting point. Terylene melts at 249° C. One reads of different melting points; much depends on how the measurement is made; *e.g.*, if on an electrically heated plate it may seem different from melting in a tube. Some people quote 260° C. The figure of 249° C. is conservative but at least the fibre will always be solid at that temperature. It has a density higher than that of nylon, and its handle may be preferred.

CHAPTER 26

SNAP-BACK FIBRES

LYCRA, VYRENE, SPANZELLE

The fibres discussed in this chapter are those which resemble rubber in that they have a high extensibility and highly retractive forces which derive from their chemical nature. Some stretch nylon yarns such as Helanca have high stretch and recovery but these properties are due to special configurations of their filaments brought about by various devices such as special forms of crimping and twisting; the individual filaments of such yarns are not elastic in the sense that rubber is.

Fibres which have an extension at break in excess of 200 per cent, and have also the property of rapid recovery when the tension is released, are known as elastomers. Undrawn nylon has an extensibility of several hundred per cent, but practically no recovery and is not an elastomer. First attempts to make true rubber-like fibres centred on the modification of nylon; these were not completely successful and this line of attack has been abandoned. The polyurethane fibres have been more satisfactory and some of them are now on the market. In Britain, Courtaulds (Elastomeric Fibres Ltd. of Coventry) make Spanzelle, a multi-filament yarn in which the filaments have been fused together. Vyrene is made by the Dunlop Rubber Co.; du Pont were already making Lycra at Maydown in Northern Ireland at the end of 1969; Glospan is made by the Globe Elastic Thread Co. Ltd., and it also is a fused multifil yarn and so is Blue C Elura made by Polythane Fibres Ltd. Snap-back fibres originated in the U.S.A.; the first two were du Pont's Lycra and the U.S. Rubber Co's Vyrene. Also in the U.S.A. is Monsanto's Blue C Elura, another fused multifil. Glospan is made there by the Globe Manufacturing Co. and Spandelle by Firestone, who were associated with Courtaulds in the manufacture of Spanzelle. In 1971 Courtaulds reported that Spanzelle was doing better and profits increasing. In 1972 they reported further and continuing progress. The fibres are all very similar, despite the ramifications of the commercial interests; they are an American development, and those that are made in Britain have been made with American help. In 1968 similar fibres were also being made in West Germany, the Netherlands and Japan, again with American help. The fibres are known generically as spandex fibres. Those synthetic fibres that have

already been discussed—*i.e.*, the polyamides, polyureas and polyesters—are all condensation polymers. Those organic fibres still to be discussed are all vinyl-type addition polymers. The polyurethanes do not fit at all satisfyingly into either group. So, perhaps, here between the two main groups is as good a place as any to deal with them.

MODIFIED NYLON

Although the elastic nylons have been abandoned, they were of considerable academic interest. The general idea was to make use of the high extensibility of undrawn nylon, but by the inclusion of bulky side groups to reduce hydrogen bonding and make it impossible for the nylon molecules to fit together nicely and find restful positions; instead they were bulky, ungainly, and when stretched were always in a state of strain so that when tension was released they reverted to their original positions and the nylon retracted.

Nylon 610 made from hexamethylene diamine and sebacic acid was the basis, but a part of the hexamethylene diamine was replaced by a substituted diamine carrying butyl or *isobutyl* groups, which are very bulky. The product had a tenacity in excess of 1 gram per denier and an extensibility of up to 400 per cent and a rapid recovery of 95-99 per cent; it was certainly an elastomer. Another method that was used was the after-treatment of nylon 66 with formaldehyde and methyl alcohol; this introduced methylene cross-linkages and methoxymethyl side groups. These bulky side groups and the cross-linkages both contributed to retraction from stretch and the product was rubbery, but it was not very stable.

Such fibres were never quite right; they were either unstable chemically or showed excessive stress decay; the first meant that garments made from them would not withstand repeated hot water washing, the second that they would gradually get bigger and sag. It is a pity that this line of attack was never quite successful; the nylon manufacturers poured millions into it. If it ever is completed, the products will probably be much stronger than the polyurethane spandex fibres.

POLYURETHANE FIBRE—PERLON U

Modern spandex fibres are polyurethanes, but the first polyurethane fibre to be spun (first spun in Germany during World War II) was not an elastic yarn but an ordinary "hard" yarn, rather like

This unit together with any unreacted di-isocyanate is next reacted with some diamine, possibly hydrazine NH_2NH_2 , and in order to prevent the reaction going too far a little monamine is added as a stabiliser. The final stage is carried out in dimethyl formamide solution and then the Lycra is dry-spun from this solution. The last reaction may be represented



In this last formula the "soft" linkages will consist of polybutylene ether from the original tetrahydrofuran. But the synthesis is complicated and the product is doubtless complex. Any simple written equations will do no more than indicate in a general way what is happening.

Vyrene. The U.S. Rubber Co. have described some of their polyurethanes in U.S. Patent 2,751,363 (1956). According to this a mixture of ethylene and propylene glycols is esterified with adipic acid using excess of the glycols so that there results a polyester with terminal hydroxyl (not carboxylic acid) end groups; this is made as a low polymer with a molecular weight of about 2,000. This polyester is reacted at about 120° C. with *p,p'*-diphenylmethane di-isocyanate using 2 moles of the latter to one of the polyester which is in fact a linear polyurethane having terminal isocyanate groups.



Ethylene glycol.

Propylene glycol.

Adipic acid.



Polyester of molecular weight 1,652 (or shortly HOROH),



Diphenylmethane di-isocyanate.



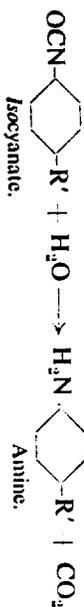
Polyester:

Diphenylmethane di-isocyanate.



Polyurethane (so-called polyester di-isocyanate).

This liquid intermediate is then reacted with a small quantity of water which converts some, but not all, of the isocyanate groups to amine groups:

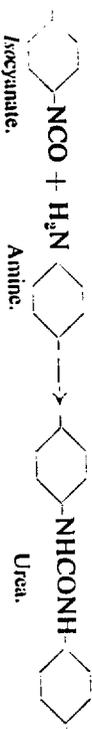


Isocyanate.

Amine.

(only a fragment of the molecule is depicted). At this stage the polymer is spun into fibre. The unique feature of Vyrene is that the final cross-linking reaction takes place after the fibre has been spun.

The so-formed amine groups are very reactive and react eagerly with unchanged isocyanate groups to form urea bonds:



Isocyanate.

Amine.

Urea.

This reaction gives a cross-linked product which is no longer liquid but is a gum which resembles uncured sheet raw rubber. The gum is "cured" (this increases the degree of polymerisation) by heating under pressure at 130° C. for 1 hr. There is nothing very simple about this, the final polymer contains urethane, urea and ester linkages whilst the chain includes ethylene, propylene, tetramethylene and diphenylmethane groups. U.S. Rubber Co. define one of their polyurethane polymers as "an elastomeric polymeric cross-linked chain-extended di-isocyanate-modified polyester or polyester-amide".

Despite the complexities of the above two syntheses it is possible to see that each consists of four essential steps and that there is really a very close parallelism between the syntheses of Lycra and Vyrene. Perhaps the Table on page 492 may clarify this.

The Federal Trade Commission defines spandex yarns as "a manufactured fiber in which the fiber-forming substance is a long chain synthetic polymer comprised of at least 85 per cent of a segmented polyurethane". It seems to be clear that they are essentially polyurethanes but that in between the urethane groups there are long chains which may be polyglycols, polyesters or polyamides or copolymers of them.

Stage of synthesis.	Essential feature of stage.	In detail in the synthesis of:	
1	Preparation of a low linear polymer with terminal hydroxyl groups.	Lyera.	Yrene.
2	The low polymer is reacted with excess of a di-isocyanate to give a polyurethane which has terminal isocyanate groups.	The low polymer is polybutylene glycol. Toluene-2,4-di-isocyanate is used.	The low polymer is a polyester made with excess of ethylene and propylene glycols (excess so as to ensure terminal hydroxyl groups). Diphenylmethane diisocyanate is used.
3	Water, in deficiency, is added to convert some of the terminal isocyanate groups to amine groups.	At this stage a linear prepolymer with terminal isocyanate and amine groups.	At this stage a linear polymer with terminal isocyanate and amine groups.
4	The linear polymer is cured by heating. Amine and isocyanate groups react to give urea cross-linkages. The abundance of cross-linkages give the snap-back property.	The resulting cross-linked polymer is Lyera. It contains ether (from the glycol) urethane and urea linkages and probably others.	The resulting cross-linked polymer is Yrene. It contains ester (from the first stage) urethane and urea linkages and probably others.

Properties of Spandex Fibres

The stretch before break of Lyera yarn is from 520 to 610 per cent (rubber 760 per cent); Lyera can be stretched to six or seven times its original length, rubber to 8½ times. The breaking strength of Lyera is about 0.7 gram per denier equivalent to about 4.5 grams per breaking denier; that of rubber is 0.25 gram per denier equivalent to 2.3 grams per breaking denier. At a given stretch the recovery of Lyera is inferior to that of rubber; recovery from a 50 per cent elongation is only 93.5-96 per cent; it might be thought that this was a serious defect. Lyera has an advantage over rubber in being white and dyeable. It has good resistance to chemicals; it is degraded and yellowed by hypochlorites but will withstand swimming pool concentrations (0.5 p.p.m. available chlorine maximum); it withstands the action of perspiration and of sun-tan and other cosmetic oils (rubber is not very good against oil). Lyera can be washed repeatedly in washing machines at 60° C. and tumble-dried

at 80° C., but bleaches that contain chlorine must be avoided as they degrade and yellow the fibre.

Lyera yarn is spun as multifilament but the filaments are joined together into what is in effect a monofil. Fig. 172 illustrates the filament adhesion. Yrene is a monofil. Deniers available range from 70 to 560, 420 being the most popular. Moisture regain is 0.3 per cent, specific gravity about unity, melting point is 250° C. but sticking occurs at 175° G. The fibre is soluble in boiling dimethyl formamide. Sometimes Rubber Gauge is used instead of Denier to express the size of a spandex thread. An approximate relation between them is: Rubber Gauge = $\frac{2350}{\sqrt{\text{Denier}}}$, e.g., 100 Rubber Thread Gauge = 560 denier, 200 Rubber Thread Gauge = 140 denier. This is for cut rubber. For extruded rubber the gauge number is about 10 per cent less, e.g., 180 extruded Rubber Thread Gauge = 140 denier.

Dyeing

Direct dyes as a rule have no affinity for Lyera and are not used. Disperse dyes have good affinity, so have acid and basic dyes. Lyera is usually dyed in combination with nylon and disperse dyes

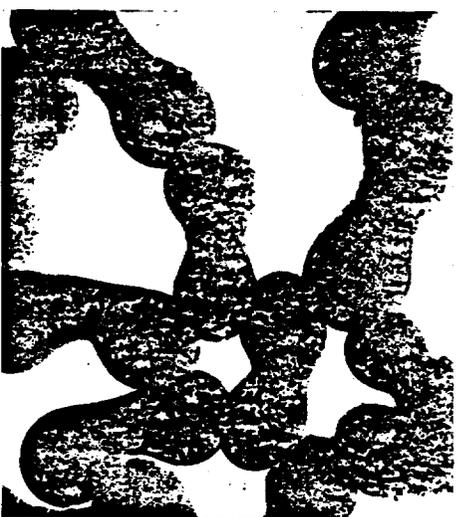


Fig. 172.—Photomicrograph showing cross-section of Lyera filaments. Adhesion between them can be seen. Magnification $\times 110$ —the filaments are very big.

[E. I. du Pont de Nemours & Co.]

CHAPTER 27

VINYLON AND VINYLON HH

It has long been known that vinyl chloride, which is a colourless liquid, would polymerise readily and that the polymer could be drawn out into long filaments. Naturally, this attracted much attention, and many chemists tried to make useful fibres from polymeric vinyl chloride and acetate too, but the fibres they made were too weak to be useful. In 1933 E. W. Rugeley, T. A. Feild and J. F. Conlon tackled the problem again, this time with success. They obtained useful fibres, to which the name "Vinylon" was given, and assigned the patent rights of the process to the Carbide and Carbon Chemicals Corporation in America. This firm made the polymer in the form of a white, fluffy powder, but did not spin it. The spinning was performed by the American Viscose Corporation, who in 1939 converted the polymeric powder into textile filaments. It is interesting to note that Vinylon, which is like nylon in that it is a true synthetic fibre, made its appearance at almost the same time. For thousands of years Man pursued textile crafts without producing a synthetic fibre; then two such fibres, quite distinct from each other, appeared in a period of two years.

Chemical Structure

Vinylon is a co-polymer of vinyl chloride (88 per cent) and vinyl acetate (12 per cent). It is called a co-polymer because the two are polymerised together. Either vinyl chloride or vinyl acetate will polymerise separately, but the polymers that result have their limitations for forming fibres. Polyvinyl chloride alone is a hard, tough, water-white resin which must be plasticised for extrusion purposes because it has a low decomposition temperature. Polyvinyl acetate is a clear resin of good acetone solubility, but one which softens at temperatures not much higher than room. Mixtures of polyvinyl chloride and polyvinyl acetate have not displayed any very promising properties, but resins (co-polymers) produced by the simultaneous polymerisation of mixtures of monomeric vinyl chloride and monomeric vinyl acetate have quite different and very useful properties. The function of the vinyl acetate is to plasticise the vinyl chloride internally—*i.e.*, in the same molecule. The reaction may be represented:



The most suitable polymers for making Vinylon fibres are those that have molecular weights in the range of 10,000–28,000. If the molecular weight is lower than 10,000 the fibres are weak, for very long molecules are necessary to give *any* strong fibres, and if the molecular weight is higher than 28,000 the polymer is insoluble in the solvents, from solution in which it is usually spun.

Manufacture

The co-polymerisation of vinyl chloride and vinyl acetate is effected by heating, probably in the presence of a catalyst of the aluminium chloride, AlCl_3 , or boron trifluoride, BF_3 , type. The polymer is dissolved in a solvent, acetone, or its homologue methyl ethyl ketone (M.E.K.), and a solution which contains 23 per cent by weight of the co-polymer is made. This is filtered and de-aerated, and then extruded through fine orifices by the pressure of a pump. The "filaments" emerge into a counter-current of warm air which evaporates the acetone so that the filaments solidify and can be wound. The process of spinning is very similar to that used in the manufacture of cellulose acetate. The air from the spinning cabinets which contains acetone is drawn through ducts to a recovery plant, where it may be scrubbed in water and the solutions of acetone in water gradually concentrated. When it is spun, Vinylon is weak and has to be oriented by stretching in the same way as nylon. It is first twisted in the wet state, and is then given a stretch of about 800 per cent—*i.e.*, it is stretched to nine times its original length. The yarn before stretching has a tenacity of about 0.8 gram per denier and after stretching one of 3.4 grams per denier. If a dull yarn is required, a pigment such as titanium oxide may be incorporated in the dope of vinyl resin and acetone.

Properties

Vinylon yarn has a tenacity of about 3.4 grams per denier and an elongation at break of 18 per cent. It is as strong wet as dry, probably because it is very resistant to the action of water. The moisture content at standard conditions is less than 0.5 per cent. If this is compared with the value of 12 per cent for viscose rayon the difference will be very evident.

Because Vinylon is a stretched yarn, the filaments are usually very

fine—e.g., a yarn of 40 denier may have twenty-eight filaments, i.e., a filament denier of 1.43. Its specific gravity is 1.37, which is not very different from that of cellulose acetate (1.33) or wool (1.32), but is considerably lower than that of viscose (1.52) and higher than that of nylon (1.14). Vinyon is a non-conductor of electricity.

The fibre is thermoplastic at temperatures over 65–70° C. When heated to 150° C. it becomes tacky and begins to melt—a very serious defect. It is unattacked by bacteria, fungi and the larvae of moths and carpet beetles. Chemically it is very stable, and resists attack by even high concentrations of alkalis and mineral acids, although it is softened at high temperatures by acetic acid.

Under the microscope, the fibre resembles mercerised cotton, with a lumen-like channel appearing to run through the middle of the filament. This is an optical illusion, for the filament is solid, and is caused by the peculiar cross-section of the filaments, which is flat and slightly dumb-bell shaped (Fig. 173). The "lumen" does not show more than faintly in this picture.

Vinyon is satisfactorily stable to the action of sunlight.

Dyeing

Dyeing is not easy, owing to the very high resistance of the material to water, and special dyeing assistants which temporarily soften the surface of the filament, and so make it more penetrable, have been used. A series of dyestuffs has been marketed for dyeing Vinyon, under the name Calcovins. It may also be dyed satisfactorily with dispersed colours of the cellulose acetate type. Owing to the thermoplasticity of Vinyon, its maximum safe dyeing temperature is 60° C. The use of pigments in the dope might be expected to give good bright colours, and so avoid the dyeing difficulties, but the use of pigmented dope is not always attractive to the manufacturer, as he has to segregate carefully the different colours; pipe-lines that have been used for a red dope will take a long time to become completely free from red. Perhaps the best method is to spin three basic colours—a red, a blue and a yellow—and modify these by subsequent dyeing of the filaments to obtain the large range of colours that the market demands.

Vinyon, because of its very considerable content of chlorine, will not support combustion, although it will burn in a flame.

Uses

Vinyon has found very considerable application. Its superlative chemical resistance makes it very suitable for use in filter-pads and in protective clothing for chemical workers. Its resistance to water has

enabled it to be used for fishing-lines and nets. In fabric form it effectively replaced No. 10 silk bolting cloth as a screen printing material when this became unavailable. Other uses include felts, sewing-threads and twines, and ladies' gloves which have been made from warp-knitted Vinyon fabric. Its great defect of having such a low melting point means that it cannot be used for materials and

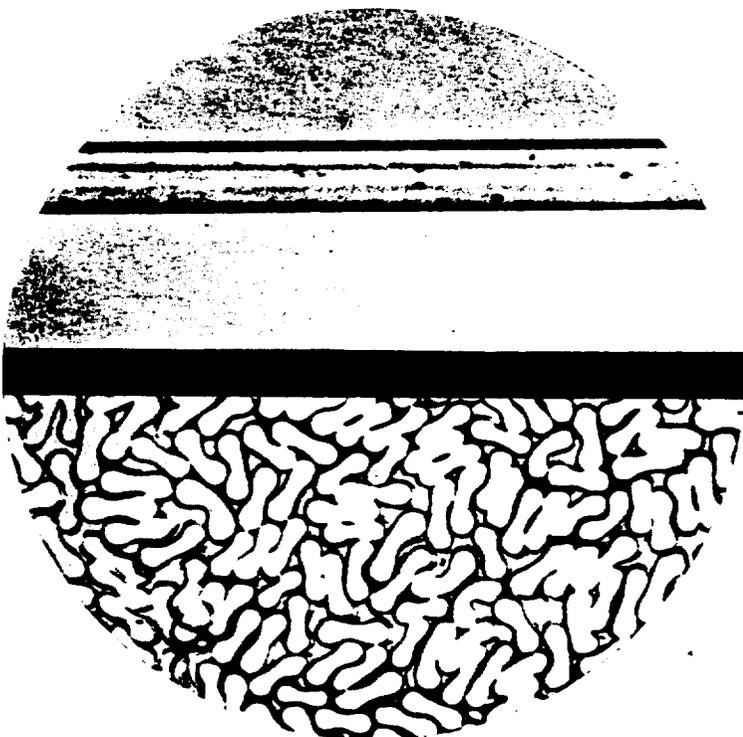


Fig. 173.—Photomicrograph of Vinyon filaments ($\times 500$)

garments that normally are laundered, and apart from this its very poor absorption of moisture makes it unsuitable for underwear. Most important applications are felts, carpets and filter fabrics.

It has been used almost exclusively in continuous filament form, although a little staple fibre has been made. The unusual properties of Vinyon have made it possible to use it for purposes for which most textiles are unsuitable, but, on the other hand, they have prevented it being used for the more common purposes. Vinyon N and

Dynel, which are developments of Vinyon, have probably now taken over most of the uses that Vinyon promised to fill.

VINYON HH

Vinyon HH is a staple fibre that is spun by the American Viscose Corporation from a solution of co-polymerised vinyl chloride and vinyl acetate, *i.e.*, it is similar in chemical composition to the original Vinyon. It is made in staple form only. In 1962 Vinyon HH was still being made by the American Viscose Corporation and is sold at 80 cents per lb.

Manufacture

The co-polymer is dissolved in a solvent, probably acetone, and dry spun. The method of spinning is similar in principle to that used for cellulose acetate. The filaments are cut to staple and opened before they are shipped. Vinyon HH is made in the following sizes:

2 denier	• • • • •	3-5 in.
3 "	• • • • •	1-5 in.
5.5 "	• • • • •	1-5 in.

Properties

Vinyon HH has a low strength (0.6-0.8 gram per denier) and a high extensibility. It has exceptional water resistance and is practically as strong when wet as dry; it absorbs less than 0.1 per cent moisture. It will not grow bacteria, moulds or fungi and will not support combustion; it has the high dielectric strength of 650 volts per mil. Specific gravity is about 1.35.

Chemical Resistance. Its chemical resistance is good; it is practically unaffected at room temperatures by concentrated acids such as sulphuric, nitric, hydrochloric, hydrofluoric and aqua regia; it is resistant to 30 per cent caustic soda or caustic potash solutions and is unaffected by salt solutions, cuprammonium solutions, alcohols, glycols, paraffins, petrol and mineral oils. At higher temperatures, mineral acids may char and embrittle the fibre. Examples of its resistance to sulphuric acid are given below; it can be seen that, as the temperature is raised, the concentration that the fibre will withstand falls.

Temperature (° C.).	Maximum concentration of sulphuric acid which has no noticeable chemical action on fibre (per cent).
25	95
58	80
70	75
80	65

The fibre is, however, dissolved by ketones and softened or partly dissolved by esters, ethers, aromatic hydrocarbons, and some amines and chlorinated hydrocarbons.

Effect of Heat. The most important characteristic of Vinyon HH staple fibre is its ability to soften, shrink and bond to other fibres when heated under pressure or in the presence of some solvents. Temperatures at which the fibre changes character are as follows:

Softening temperature	• • • • •	52-60° C.
Shrinkage	" "	60-66° C.
Tacky	" "	85-102° C.
Melting point	• • • • •	135-149° C.

Dyeing

Vinyon HH presents considerable difficulties; it cannot be dyed deep shades with both wash and light fastness. The best method is to apply an acetate dyestuff in a bath containing 5 per cent of a swelling agent such as *o*-hydroxydiphenyl or dibutyl phthalate, and to dye at 55° C. for three-quarters of an hour.

Uses

Spinning with Other Fibres. The low strength and high extensibility of Vinyon HH have made it a not very satisfactory fibre to spin into yarn. All-Vinyon HH gives static trouble; this can be reduced by the application of a suitable finish and the use of a static eliminator, and 100 per cent Vinyon HH has been spun experimentally to 20 s cotton counts. Blending with 25 or 50 per cent cotton or rayon is advisable for spinning on the cotton system, for which 3 denier 14 in. staple is preferred. Mixtures of Vinyon HH and wool can be spun more satisfactorily on the woollen system.

Bonding. The ability of Vinyon HH to shrink when heated in combination with other fibres is made use of in the manufacture of rubber-coated elastic fabric and of embossed carpets. The shrinkage of Vinyon HH fibres at different temperatures is as follows:

Temperature (° C.).	Shrinkage (per cent). U.S.T.
60	Nil
71	18
74	27
79	45
85	50
91	55
100	60
110	65
121	70
132	Melting range

The main use of Vinyon HH is for bonding and heat-sealing. The ability of Vinyon HH to bond to other fibres is used in making pressed felts, bonded fabrics and heat-sealable papers.

The temperature at which the bonding is carried out is important; in batch processing it should preferably not exceed the "tacky" temperature, otherwise the fabric will be unduly stiffened. In continuous bonding processes where the fabric is exposed to heat and pressure for a very short time it may be necessary to use a temperature almost as high as the melting point of Vinyon HH.

WACKER MP FIBRE

Wacker-Chemie G.m.b.H., Munich, make a fibre—MP Fibre—in which the major monomer is P.V.C. It is distributed in the U.K. by Bush, Beach and Segner Bayley Ltd., of Cheadle Hulme. According to *Zeitschrift für die gesamte Textilindustrie*, 67 (11), 879-880 (1965), Wacker's MP Fibre is parallel to Vinyon HH. The fibre is heat-sealable and weldable and probably finds most use in non-wovens. It is not intended primarily for textile spinning because of its low strength of 0.5-0.7 gm./denier, but mixed with stronger fibres it can be spun. The inclusion of 10-20 per cent Wacker MP in other fibres makes it possible to obtain products with a film-like or papery texture by varying the pressure during heating. The properties of MP Fibre are much as already described for Vinyon HH: moisture absorption is given as 0.2 to 0.4 per cent compared with 0.1 per cent for Vinyon. It becomes tacky at 70-80° C. and melts at 150-170° C. and is free-flowing at 170-180° C. Uses to which Fibre MP has been put are: in heat-sealable paper, paper tea-bags, shoe linings, decorative materials and weldable wadding. The fibre is supplied as staple, usually 3 denier 40 mm. long or 5 denier 60 mm. staple. An interesting application is in carpets; ordinarily the cut edges of woven fitted carpets are reinforced with an adhesive, an operation that is disliked. But now, instead, a number of warp threads along the edge are made of Wacker MP Fibre and some in the weft too, so that demarcation between the individual carpets is possible. The edges of the carpet can be fused by heat treatment. The fibre is primarily intended for such special uses and not for traditional household textile uses where it would not withstand the usual laundering and ironing. For cleaning, perchlorethylene and trichlorethylene are not very suitable, but some fluorinated hydrocarbons can be used safely, e.g., trifluoro-trichlorethane—such products as Frigen, Calutron and Walclene. White spirit too is safe. The fibre is made from 85 per cent vinyl

chloride, 15 per cent vinyl acetate. Cost is of the order of £900 per ton. Paper makers take the fibre in 3 denier 5 mm. staple.

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Rayon Textile Monthly (Elastic Vinyon). Nov. 1942.
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Dyeing

Dyeing is the main trouble with the vinyl and vinylidene fibres; there is, of course, no gainsaying that devices have appeared whereby these difficulties have been surmounted, but the difficulties are not really removed. If, for example, some modification could be made to Orlon so that it could be dyed easily by traditional methods there is no doubt that the use of the fibre would very greatly increase. Darvan has a low dye affinity; it cannot be dyed with direct, acid, metallised or chrome dyestuffs. Dispersed dyestuffs at the boil will give pastel shades, and heavier shades such as bright red, maroon, navy and black can be obtained by azoic dyestuffs, of which β -oxynaphthoic acid is one component (*cf.* p. 453). Carriers can be used to increase the depth of shade from disperse dyes, and the cuprous ion method can be used with acid dyestuffs; *o*-phenylphenol used at 4 gm./litre or methyl salicylate (oil of wintergreen) used at 8 gm./litre are the best carriers. Vigorous after-scouring is required to remove excess dyestuff or residual carriers. The picture is familiar in outline, but so far the detail has not been filled in. Apparently the fibre can be heat-set. It can be bleached with acid hypochlorite.

Uses

Darvan's outstanding properties are good handle, resistance to sunlight and relative freedom from pilling. Intended uses were in hand-knitting yarns, sweaters, women's pile coats and in blends for tropical suitings and men's shirtings. It would probably have been made only in staple, not in continuous filament, and mostly in fine deniers. But it never has been made. It has been a good exercise in fibre technology, but no more.

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CHAPTER 38

POLYETHYLENE COURLENE, MARLEN

Like many other fibre-forming materials—for example, cellulose acetate and Saran—polyethylene was made originally as a plastic material, and only later, after it had established itself in the plastics field, was its use for fibres developed. Polyethylene resulted from research carried out by I.C.I. Ltd. on the effect of very high pressures on gases. The plastic made by I.C.I. Ltd. is given the name "Alkathene".

Chemical Nature

When ethylene gas is subjected to high pressures and temperatures, it polymerises and forms a solid. The mechanism is one of addition polymerisation, very similar to that whereby Vinyon and Saran are formed. The reaction by which polythene is produced is as follows:



The higher the pressure to which it is subjected, the higher the molecular weight of the polymer.

Manufacture

Ethylene gas may be obtained by cracking petroleum or, alternatively, from alcohol. At one time alcohol was made by fermentation and ethylene was made by dehydrating the alcohol, but since the erection of oil cracking plants, ethylene has been obtained from petroleum. Indeed most of to-day's alcohol is also made from this ethylene and it is estimated that by 1964 there was only very little fermentation alcohol made; almost all of it coming from oil cracking. The ethylene is polymerised in autoclaves at 200° C. and 1,500 atmospheres pressure (about 10 tons per square inch) in the presence of a trace (0.01 per cent) of oxygen, which acts as a catalyst. The polymer (M.W. 15,000) is spun from the melt at a temperature of 300° C. through spinneret orifices of 0.1 mm. diameter into a current of cooling gas. After spinning, it is cold drawn to six times its original length. In addition to melt spinning, solvent spinning has been used but, owing to the relative insolubility of polyethylene, the solvents, of which benzene is one and xylene another, have to be

used hot. Melt spinning would appear to be a proposition much more attractive than hot solvent spinning. If the polythene has a molecular weight of 6,000 it gives filaments with a tenacity of 0.8 grams per denier, but if the molecular weight is 21,000 the tenacity is as high as 3 grams per denier. The polyethylene yarn made by Courtaulds Ltd. is known as Courlene. Several American manufacturers make polyethylene yarns, notably Reeves Bros. Inc. (Revyon) and National Plastic Products Co. (Wynene J).

Properties and Uses

Courlene has a tenacity of 2-3 grams per denier and an elongation of 40 per cent. The outstanding property of polyethylene is its chemical stability, which has proved of great value when the material, as a plastic, has been used for applying protective coatings on other material. This coating can be carried out with a Schori spray-gun. The fibre is also very resistant to microbiological attack.

From the textile standpoint, the very low melting point of 110-120° C. militates against its use for normal textile purposes; it would be quite impossible to iron it with a normally "cool" iron. It does not possess the non-flam properties of Vinylon and Saran, so it is unlikely to be used for some of the purposes for which these particular fibres have been found suitable.

Polyethylene has a very low frictional coefficient, probably because of the lack of polar chemical groups in its molecule. This gives it a waxy handle which is very noticeable; the low frictional coefficient is responsible for some of the special uses to which polythene is put. Fabric made from 500 denier monofil has been used for car upholstery; the fabric is pre-shrunk (British Pat. 673,879) to avoid shrinkage during summer use. Courlene has been woven into fabric and used for protective clothing in industries where contact with corrosive chemicals is likely. Boiler-suits made from it have proved satisfactory in a sulphuric acid plant, as have also women's overalls in a factory where acid powders are handled. The woven structure allows the fabric to breathe, and overalls made from it are more comfortable to wear than similar garments made from plastic film. Protection against chemical splashing, dust and vapour is excellent. Courlene fabrics have also been used for low-temperature filtration and for clay and sewage filtration. The U.S. Rubber Co. make a fabric (Trilok) which consists of polyethylene yarn in the warp and conventional yarns, e.g., rayon, in both warp and weft; the raw fabric is immersed in boiling water and the polyethylene yarn shrinks about 50 per cent, cocking the fabric, giving it a three-dimensional figure and a cushioning action.

Effect of Nuclear Radiation. Polyethylene is one of those fibres that become cross-linked when irradiated with cobalt-60. The effect of this cross-linking has been strikingly demonstrated in the following way:

Polyethylene normally softens at 110-115° C. and at that temperature can no longer support its own weight, but if it has previously



FIG. 205.—Irradiation with cobalt-60 increases the melting point of polyethylene. The polyethylene bottle (a) which has not been irradiated melts in an oven at 135° C.; the bottle (d) which has had a big dose of radiation does not melt in the same oven; the others intermediately.

(Strawsoda Mining and Manufacturing Co.)

been irradiated with γ -radiation or with high speed electrons it becomes rubbery rather than liquid at 110-115° C.; the cross-links restrict molecular freedom. Fig. 205 shows four polyethylene bottles that have been in an oven at 135° C. for 15 min.; the one on the left (a) has not been irradiated and has melted to a shapeless blob; the one on the right (d) has had a high dose of radiation and is

consequently able to withstand the temperature of 135° C.; the other two (b) and (c) have had smaller doses. The higher the dose of radiation, the better will the polyethylene subsequently withstand the effect of heat.

It is clearly to be seen from Fig. 205 that nuclear irradiation can modify the properties of polyethylene very significantly and that the subject has more interest than has often been thought. Some Russian work by Karpov, Yurkevich *et al.* has thrown a good deal of light on the subject. The radiation to which the fibres were exposed was expressed in rads. The rad is a unit of absorption of energy and corresponds to 100 ergs of deposited (and absorbed) energy per gram of matter. It is roughly equal to the absorbed dose when soft tissue is exposed to one roentgen of medium voltage X-rays. The millirad corresponds to a deposited energy of one-tenth of an erg per gram of matter—in the present instance, of fibre. Polyethylene filament yarn of 136 denier (or 15.1 tex or Soviet No. 66.2) was irradiated on a K-20,000 instrument at a power of 0.162 millirad per second for 12 seconds, *i.e.*, 2 millirads; and for 50 min. (500 millirads) and for intermediate times. Exposures were made both in air and in vacuum and as could have been expected the vacuum-treated were better than the air-treated samples, as shown in the following table.

Irradiation of Polyethylene

Dose in millirads.	Irradiated in air.		Irradiated in vacuum.	
	Strength of fibre (gm./denier).	Extension at break (per cent).	Strength of fibre (gm./denier).	Extension at break (per cent).
None	4.7	13	4.7	13
0.5	3.8	14	4.9	15
2	3.3	16	4.3	14
5	3.2	13	4.4	14
15	1.7	7	4.1	12
100	1.4	4	3.3	12

Resistance in vacuum may be of academic interest but it is resistance in air that is useful. In the shorter exposures there may be a little evidence (viscosity increases from 1.18 to 1.25) of some cross-linking, but there is not much in these results to encourage anybody. Thermal stability is better as was found earlier. What does show clearly (see p. 556) is that polyacrylonitrile will withstand nuclear radiation much better than polyethylene, or polypropylene

or polyamide. It is of interest to fibre specialists that some dyestuffs can be used to measure radiation doses in the range 10⁵ to 10⁸ rad. Such "dyes" are the colourless cyanides of some aminotriphenylmethanes; these develop colour when exposed to radiation, and the depth of colour can be used as a measure of the radiation dose (*Textile Processing*, Dec. 1965, pp. 30, 31).

Low-Pressure Polyethylene—MARLEX 50

It has been found that in the presence of certain catalysts (pp. 117-120), ethylene can be polymerised at temperatures and pressures that are considerably lower than those first used. Various catalysts have been suggested, notably aluminium alkyls and chromium oxide mounted on silica-alumina. The Phillips Petroleum Co. of Bartlesville, Oklahoma, have used 2.5 per cent chromium oxide mounted on silica-alumina, to polymerise ethylene in a hydrocarbon solvent at a temperature of 130-150° C. and a pressure of 450 lb./in.². The very much lower pressure necessary in the presence of the catalyst means a big capital saving on the cost of the plant. Polymers with molecular weights of 40,000 and higher have been made. One of these is called Marlex 50.

Low-pressure polyethylene has a higher density (0.96) than ordinary high pressure polyethylene (0.92) and softens at about 125° C. instead of 105° C.; its chemical resistance is slightly better and its tenacity, when spun into a monofilament, is high at 4.4 grams per denier, whereas 2.7-3.0 grams per denier is good for conventional high-pressure polyethylene. It still remains that, with a melting point of about 125-130° C., Marlex 50 is unsuited for traditional textile purposes, but it does show a significant improvement in most ways over the older material, and in view of the more moderate conditions of polymerisation it seems likely to supersede the older high-pressure polyethylene. The makers of Marlex 50 have suggested its suitability for "automobile interiors, curtains, furniture covers, tarpaulins, filter cloth, rugs, rope and fish nets".

Courlene X 3

Courlene X 3 is a polyethylene monofil that Courtaulds Ltd. have introduced with certain improved properties. Melting point is higher at 135° C. and it is more stable in boiling water—an important point for cleaning protective clothing. It is, however, still subject to a shrinkage of 12 per cent at 100° C., and allowance must be made (not easy) for this in the design of a garment. In strength

(4 grams per denier) and abrasion resistance Courlene X 3 is superior to the original Courlene. Its specific gravity is 0.96.

The improved properties of low-pressure polyethylene are due to better molecular packing of the fibre molecules and to the consequently higher degree of crystallinity of the fibre. This brings with it a higher density, strength and melting point, as well as improved resistance to chemical attack. Low-pressure polyethylene is a linear polymer (see pp. 124-125).

Complementary Polyolefine-Nylon Blends

The reader will have gathered that the properties of polyethylene and nylon are very different. The question arises as to whether blends of the two would give the best or the worst of both. The test may not yet have been made on fibres, but it has certainly been made on plastics.

In B.P. 889,354 (1962) the Continental Can Company described some blends of nylon 6 and polyethylene as plastics. A comparison of the properties of the two components was as follows:

	Polyamide (e.g., nylon 6).	Polyolefine (e.g., low-density polythene).
Chemical inertness	Good	Good
Toughness and flexibility	Good	Good
Ease of fabrication	Good	Good
Cost	Temperature range for extrusion is narrow	Good
Permeability to water	High	Low
Permeability to lower alcohols	High	Low
Permeability to hydrocarbons	High	Low
Permeability to esters, ketones, etc.	Low	High
Printability	Good	High, unless pre-treated by fluffing or chemically
Discoloration on extrusion	Yellows	None

The two polymers have no common solvent, and the only way of making an intimate mixture is in the melt. Provided that a high pressure, preferably of 130 atmospheres, was maintained, that each of the two components was present to the extent of at least 5 per cent (this is to give impermeability, not uniformity) and that the melt was kneaded with a shearing action and with turbulence, suitably obtained by the use of mixing screws, then a homogeneous melt was obtained. A blend of 20 per cent nylon 6 and 80 per cent polyethylene was almost impervious to esters such as in oil of wintergreen

to hydrocarbons such as heptane. The use of similar blends for fibres is a development that we shall probably see.

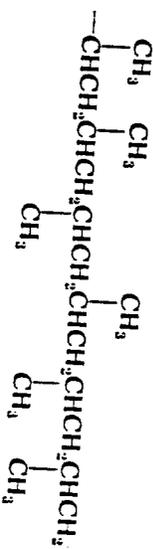
Application to Wool

Plastic materials are sometimes applied to wool in order to cover its scale structure and thereby make the wool unshrinkable. There are various ways in which a measure of shrink-resistance can be obtained, and these have been discussed in the author's "Wool Shrinkage and its Prevention". The application of a plastic to the fibre is not altogether good, because it alters the handle of the wool fibre. Warmth and softness of handle are the two most valuable attributes of wool; there is no fibre (excepting goat and rabbit hairs) which are essentially the same) to compare with it. Perhaps the polyolefines with their low frictional coefficients and smoothness of handle are less suitable than most plastics to put on to wool. It has been shown by Baldwin, Barr and Speakman at Leeds that if a resin is to be applied to wool it is better to apply it in the form of a monomer and to polymerise it on the wool fibre, rather than to apply the already formed polymer to the wool, because much better uniformity of application and better fastness are obtained by the former method. In 1962, Wolfram and Speakman formed polymethylene on wool. They impregnated the wool with a 0.1 per cent solution of copper chloride catalyst dissolved in methyl alcohol, dried the wool with the catalyst in it and then put it in a 1.4 per cent solution of diazomethane in ether. After 20 min. treatment 3 per cent of polymethylene had formed on this fibre and after 2 hr. treatment 7 per cent. Whereas untreated wool shrank 32 per cent in area under a standard milling treatment, wool with 3 per cent polymer shrank only 10 per cent and with 7 per cent polymer only 3-4 per cent. The formation of polymethylene from diazomethane may be represented:



The formula of polymethylene is essentially the same as that of polyethylene $\left[-\text{CH}_2\text{CH}_2- \right]_n$, but the former has the advantage as an additive to wool in that it can be made without the application of high temperatures and pressures. Perhaps this application points the way to the use of polymethylene as a fibre itself; it might well constitute an ideal form of polyethylene.

here and there with the methyl groups, and because the bulges on different molecules occur at different intervals the molecules cannot pack snugly together; their assembly lacks cohesiveness and cannot crystallise; instead of a solid plastic it constitutes a viscous liquid or grease. This state of affairs could not obtain with ethylene because this olefine has no side-chains and so there was little opportunity for irregularity. Propylene with its methyl side-chains had every opportunity to form irregular or atactic polymers of the type shown above. It was only when methods of controlled propagation became available as the result of work by Ziegler and Natta that isotactic polypropylene could be made. In the isotactic polymer all the methyl groups are arranged in very orderly fashion and they all lie on the same side of the plane of the main carbon chain. Fig. 45 (p. 115) represents atactic polypropylene (not fibre-forming because it is too irregular in structure for the molecules to line up nicely) and Fig. 46 (p. 116) represents isotactic polypropylene which is fibre-forming. In both Figures the plane of reference is that in which the zig-zag main carbon chain lies. More simply, but not quite so informatively, we can represent atactic (not fibre-forming) polypropylene:



and isotactic (fibre-forming) polypropylene as:



Isotactic polypropylene is stereoregular, atactic polypropylene is stereo-irregular.

Catalytic Polymerisation. Exactly what catalysts are used in the commercial manufacture of isotactic polypropylene is not known; nearly all the information available is what can be gleaned from a study of patent specifications, and it is evident from these that a large number of patent specifications, and it is evident from these that a so effectively that an isotactic polymer results. The general considerations relating to controlled propagation in addition polymerisations have already been discussed (pp. 115-121) and these apply directly to the polymerisation of propylene.

Conditions which probably approximate to those that are used commercially are as follows:

Ziegler catalyst: titanium trichloride, TiCl_3 (or possibly the tetrachloride TiCl_4 , which is reduced *in situ* to the lower chlorides).

Ziegler co-catalyst: aluminium triethyl, $\text{Al}(\text{C}_2\text{H}_5)_3$.

Liquid medium (solvent and diluent for propylene): heptane.

Pressure: 30 atmospheres; highly purified propylene is fed in repeatedly as pressure drops.

Temperature: 100° C.

Time of reaction: 8 hours.

Yield: solid polymer, 85-90 per cent, based on propylene used.

The crude solid is extracted with acetone to remove any low molecular weight material.

The molecular weight of the polymer is about 80,000; it is controlled by (a) the choice of polymerisation temperature and (b) additives which can terminate the reaction by combining chemically with the ends of the growing molecular chains. The tool used to measure molecular weight is intrinsic viscosity (p. 47) and it is related to the number average molecular weight (p. 41) by the relation:

$$\text{Intrinsic viscosity} = \text{Number average molecular wt.} \times 2.5 \times 10^{-5}$$

Melting point affords a measure of control of tacticity. Atactic polypropylene is only a grease. Unstressed isotactic polypropylene will melt at 165° C. Under stress with improved crystallisation, the melting point may rise.

In the polymerisation process there must be a solid phase present which may either be the catalyst itself or some solid, for example silica (or even sodium chloride), on the surface of which the catalyst is adsorbed. This solid phase adsorbs the monomer molecules one by one and orients them in an activated form in relation to the end-group of the growing polymer chain; the growing polymer chain adds on monomers one by one and each one is fed to it in a special orientation by the catalyst. Monomer molecules enter one after another between the catalyst and the polymer chain, tagging on to the chain. The catalyst, in effect, acts as a template which determines the shape of the growing polymer chain by a series of repetitive actions carried out at a speed by comparison with which any man-made mass production repetitive process is a laboured crawl. The solid phase is essential to hold the monomer molecules in a defined

position so that they all enter the chain, facing the same way. If the same point, the same molecule of catalyst, presents a thousand monomer molecules one after another, and one side of the monomer molecule will fit into the catalyst molecule like a ball into a socket, but not the other side which we can imagine as flat, then it is easy to understand why monomer molecule after molecule is presented in the same right hand (or left hand as the case may be, but always the same) way. Ball and socket, lock and key, or template, or whichever way you look at it, the solid geometry of the final polymer chain is determined by the solid geometry of the monomer and catalyst molecules, and the catalyst molecules are anchored to (or adsorbed on to) or form the surface of some really solid base. Could you unlock a door, even with the right key, if the screws had come loose and the lock was no longer firmly fixed to the door? The polypropylene molecule grows like a wool fibre does, *i.e.*, from the root end.

Spinning and Drawing. The polymer from which low molecular weight material has been dissolved out is melted, and spun by gear pump pressure through spinnerets. Melt spinning is usual, partly because it is cheap, mainly because polypropylene of high D.P. is difficult to dissolve. The polymer before spinning is about 50 per cent crystalline; after having been spun, the fibre has a 33 per cent crystallinity to 47 per cent; then it is annealed, *i.e.*, given a final heat treatment in which the higher temperature increases the mobility of the polymer molecules and gives them an opportunity to re-arrange themselves a bit and pack together better; this increases the crystallinity to 68 per cent. During the spinning the polymer becomes birefringent as would be expected from the orientation induced by the traction of the jet, and the degree of birefringence is increased by the drawing process, but the highest value obtained (see p. 79) is 0.035, whereas "theoretically" it could be 0.067. This discrepancy is interpreted as indicating that the molecules never open out completely but exist in a stable helical form.

Most of the polypropylene fibre that was spun at first was monofilament, but multifilament is now the main product.

Properties

Mechanical. Polypropylene is like all other highly stretched fibres in that its breaking load and breaking extension can be controlled, one at the expense of the other, by altering the degree of stretch to

which the fibre is subjected in manufacture. Tenacity is about 8.5-9.0 grams per denier and extension at break about 17-20 per cent; in these respects the fibre is excellent. Knotted strength is high, a measure of the transverse strength of the fibre. Impact strength is also high; the fibre can absorb energy. Elastic recovery is as follows: if a 2 per cent extension is held for 30 sec. and then released there is 91 per cent immediate recovery and 9 per cent delayed recovery; if the 2 per cent stretch is held for 3 min. then on release the immediate recovery is 82 per cent and the delayed recovery 18 per cent; if it is held for 6 min. then recovery within 1 sec. is 45 per cent (for comparison Terylene will recover 85 per cent of its stretch under similar conditions), but within 100 sec. it is 92 per cent.

Static Electricity. Like other hydrophobic fibres, polypropylene will develop static charges; its tendency to do this is very great because of its negligible moisture regain.

Specific Gravity. Very low at 0.90 to 0.92 depending on the degree of tacticity; polypropylene is the lightest of all commercial fibres.

Chemical Resistance. Generally excellent. Acids and alkalis have very little effect on polypropylene; 1 week in 20 per cent caustic soda at 70° C. (destroys Terylene) or in conc. hydrochloric acid at 20° C. (destroys nylon) has practically no effect. 50 per cent nitric or sulphuric acid causes a little discoloration and on lengthy immersion of the order of days, some loss of strength. Polypropylene is insoluble in cold organic solvents, but will dissolve in hot decalin and tetralin or in boiling tetrachlorethane, whilst trichloroethylene at the boil causes heavy shrinkage. Strong oxidising agents such as hydrogen peroxide will attack the fibre. Liability to oxidative degradation may prove to be a serious defect in the fibre; there may be vulnerable spots in its structure which will be attacked by air.

Moisture Regain. Practically nil, less than 0.05 per cent. Tenacity and extension are the same "wet" as dry. The low compatibility for moisture will not enhance the value of the fibre for apparel.

Abrasion. Resistance to abrasion is good. The fabric does not "pill" and this is probably a reflection of its good resistance to abrasion. Wool/polypropylene blends will pill but if the pills are examined they are found to consist entirely of wool. Whether the blending of polypropylene with wool has any effect on the tendency of the wool to pill is not known; it is unlikely that it would reduce it, but not impossible that it might increase it.

Effect of Heat. Melting point is about 165° C., softening point about 155° C., *i.e.*, too low for safe ironing. For comparison Perlon is about 215° C. and nylon about 260° C. The highly oriented (but not the undrawn) fibre is very resistant to extreme cold, and keeps its strength down to -100° C., a property which might find special uses for it.

Effect of Light. Polypropylene may be sensitive to oxidation initiated by the action of light; apparently there may be a few weak spots in the fibre, even although the main polymer chains are unaffected. Its resistance can be improved by the application of antioxidants and radiation absorbents and some such stabiliser is included in Ulstron fibre.

Colour. Colourless.

Resistance to Nuclear Radiation. The tests made by a Russian team on polyethylene (see p. 604 for details) were also made on polypropylene of 270 denier and gave the following results:

Irradiation of Polypropylene

Dose in millirads.	Irradiated in air.		Irradiated in vacuum.	
	Strength (gm./denier).	Extension (per cent).	Strength (gm./denier).	Extension (per cent).
None	2.3	9	2.3	9
0.5	2.4	18	2.4	13
2	2.7	16	2.8	16
5	2.7	13	2.4	14
15	1.6	11	2.1	16
100	1.0	4	1.6	16

There is a marked increase in fibre extensibility for low exposures; there is a significant increase in strength for exposures of the order of 2-5 millirads. There is a beneficial structural change that reveals itself in the increase of both tenacity and elongation at break. It is very common for one to be increased at the expense of the other, but the increase in *both* is unusual. How it happens we cannot be sure. Some would say that the nuclear particles knock out hydrogen atoms from the molecular chains and that when two such atoms near together but on different chains are lost, then cross-linking occurs. But the author is not so sure; cross-linking improves true elasticity, *i.e.*, recovery from stretch, but it does not usually increase extensibility. There is room for more work here; there is an indication at the start of it that the results may be of worthwhile physical improvements.

Dyeing

Polypropylene originally presented a real problem to the dyer; there are no polar groups in the structure to which dye molecules are attracted. At first, the only satisfactory method of coloration was the inclusion of pigment in the material to be spun, that is in the melt; this has given excellent results on polyethylene and proved useful on polypropylene. It does, of course, restrict the number of available shades, it is costly, it is only worth the spinner's while if he can get a really long run on each colour, it is useless for small quantities, and it means that the weaver or knitter must hold much larger stocks of raw cloth than he need do if he could send it to the dyer to be dyed in any required shade.

One method that has been tried to improve the dyeability of (uncoloured) polypropylene has been to graft side-chains of polymethyl methacrylate on to it; these contain polar groups and afford sites for dyestuff molecules to be adsorbed, and at the same time they give some moisture compatibility so that the moisture regain of the fibre is increased. All along the polypropylene chain there are tertiary carbon atoms (those to which the methyl side-chains are attached) and the single hydrogen atom that is attached to each of these has a little more reactivity than, for example, the hydrogen atoms in a typical methyl group. In particular the tertiary carbon atoms can be oxidised with oxygen or even air at temperatures of 70-80° C. and a pressure of about 3 atmospheres. When they have been so oxidised the tertiary carbon atoms on the polymer backbone will react with monomeric methyl methacrylate which forms branches of its polymer on the polypropylene chain. The side-chains form a combined hydrophilic layer some 10-100 μ thick on the polypropylene surface. It is noteworthy that isotactic polymer can be grafted-polymerised only on the surface, whereas atactic polypropylene, because of its greater accessibility, can be grafted-polymerised throughout its mass. Another possibility that has received consideration is that of high energy irradiation, for example by bombardment with γ -rays from cobalt-60. However, these methods are a long way from fruition and at present they do not seem to be very practicable. It may be that the controlled propagation method that is used for isotactic polymerisation has an inherent disadvantage in that it cuts out the possibility of co-polymerisation of the propylene with some more polar monomer, and brings the need for two-stage polymerisation: (1) isotactic polymerisation of the propylene; (2) separate grafting of polar groups on to the backbone of the isotactic

Meraklon DR (D for dyeable, R for resilient)
 Meraklon DL (D for dyeable, L for lustrous, *i.e.*, bright)
 Meraklon DO (D for dyeable, O for opaque or dull).

All three are dyed substantially similarly, but DR is a little less dyeable than the other two, and when it has been dyed its light fastness is not so good. There is a bit of undisclosed "know-how" about these dyeings and, in particular, a Montecatini product known as "Dispergal SCL-G" must be present in the dyebath and in the wash water, if a dyeing with a good light fastness is to be obtained. Given that the use of this proprietary substance is necessary, the rest of the dyeing operation is straightforward. The fibre is scoured in a solution of a non-ionic detergent and soda ash (0.1 per cent of each). But if a heavy shade is required then the preliminary scour is done in detergent and formic acid, instead of soda ash. Dyeing is carried out with acid dyes and a typical dyebath will be made up as follows (all the percentages are on the weight of Meraklon fibre that is being dyed):

Water: as much as required, probably about 30 times the weight of the fibre, *i.e.*, liquor : goods ratio of 30 : 1.
 Acid dyestuff: 1 per cent (for medium shade).
 "Dispergal SCL-G": 6 per cent.
 Anhydrous sodium sulphate: 5 per cent.
 30 per cent acetic acid: 4 per cent.

The temperature is raised to the boil over 30 min., kept at the boil for 30 min., then 3 per cent formic acid is added to complete the exhaustion (all the dye taken up by the fibre, so that the dyebath is now almost colourless), and dyeing is continued for a further 30 min. at the boil. The wash off liquor must contain 0.1 per cent "Dispergal SCL-G". A fairly long dyeing at the boil is essential to give good wet fastness, probably to drive the dye right into the fibre. Other groups of dyestuffs can be used in acid-dyeable Meraklon, and I.C.I. note the following:

1. Procion metal-complex dyes
2. Chrome dyes for blacks
3. Reactive dyes especially for bright self-colours.

Which is used will depend to some extent on the light fastness required. The Nylomine range of acid (anionic) dyes gives very fair results, and so far as concerns light fastness these are better than the Procion reactive dyes on this particular fibre.

It is clear that very great progress has been made. The Italians have done well with polypropylene: Natta first made the isotactic polymer, and now the Montecatini scientists have found out how to make it dyeable—a great achievement.

Uses

For industrial uses, dyeing of a fibre is often unnecessary, and it may be that polypropylene fibres will find more use in industry than in the home for some time to come; the fibre is already being made into ropes and for this use its great strength, resistance to abrasion and its negligible affinity for water should stand it in good stead; ordinary Manila ropes swell and get very heavy and unwieldy when used in water; polypropylene ropes will not.

For a given breaking load, polypropylene and Terylene ropes are very similar in diameter, but the polypropylene rope will be perhaps 20 per cent lighter and will cost only half as much. Ropes that are lost overboard will float if made of polypropylene and there is a chance that they may be retrieved. Hitherto the fishermen have looked a bit askance at synthetic fibre ropes that cost three or four times as much as Manila, even if they did last ten times as long; too often ropes are lost so that their potential longevity is only of academic interest. Perhaps ropes that will float will have a real life that will be longer. Furthermore, the chance that a rope will foul the propeller of a boat is much less if the rope is a floater and not a sinker. But if a floating rope is lost it may foul the propellers of other boats. Baler twine of great strength and durability is another new product that has been made from polypropylene; this product is made by Eastman Chemical Co. The high price of jute (it has risen by 50 per cent since 1962) is allowing polypropylene to nibble at its market. This nibbling may grow into something more serious.

Fishnets are already made of Ulstron. Lightness, negligible moisture regain, high strength, and probably a fairly low cost are favourable. The fibre is liable to a certain amount of creep under heavy loads, and this can affect mesh size. Large scale fishing trials are in progress.

One fantastic use that has been investigated for polypropylene fibre is as artificial seaweed. The idea apparently came from Denmark, and I.C.I. took out a licence and carried out large-scale tests at Bournemouth, on the North-East coast and in Dorset. The basic idea was that the fibre was made into fronds which were planted offshore to prevent beach erosion. However, I.C.I. have discon-

tinued their work in this direction. It might be a more attractive proposition to import the giant Pacific kelp *Macrocystis* and let it grow off our shores. In fact, this was suggested a long time ago so that the kelp could provide an abundant source of raw material for alginate extraction. The idea was turned down on the grounds that the kelp might grow too rampantly and choke our harbours. It might be worth reconsideration today.

Carpets are another outlet for which polypropylene is being used: it is used as the pile. One of the factors that is important in the behaviour of a carpet is for how long a time the height of pile is maintained; it should not be quickly flattened nor worn away. Nylon pile carpets are very popular in America and have good pile length retention properties and it is of interest that a carpet pile made of 50/50 wool/polypropylene behaves nearly as well, as the following figures illustrate.

Pile fibre.	Percentage of pile height retained after		
	2,000 treads.	5,000 treads.	10,000 treads.
Nylon	82	76	73
50/50 wool/polypropylene	74	72	70

Since the above was written polypropylene has been extensively tried for carpets; they are not a natural outlet for the fibre; they do not look as good as they might do. But polypropylene is a cheap fibre, and floor coverings made from it might do well enough for bars, snack-bars, cafes and perhaps for railway carriages. The pros and cons of polypropylene fibre for carpets may be summarised thus:

Advantages: Low cost; no static electrification or annoying shocks; lightness so that cover per lb. is high; excellent stain resistance; no piling; good strength and durability.

Disadvantages: Poor resilience; poor texture retention; poor dye pick-up; colours not bright enough; liable to melt locally if touched with a lighted cigarette.

Aesthetically polypropylene is not suitable for leisure carpets; for utility floor coverings it may have some promise.

Other uses envisaged for polypropylene are for pile and loosely constructed fabrics; velvets, voiles and so on; the high strength of polypropylene will enable it to be used in light fabric constructions.

The freedom of polypropylene fabrics from the piling scourge has already been noted.

There is no doubt that the particular suitability of polypropylene as a moulding plastic has prepared the way for its use as a fibre. By virtue of its high fluidity it will mould at low pressures by extrusion, pressing, injection or compression and the moulded products have fine detail and a high finish. The higher melting point of polypropylene, 165° C., compared with 130° C. for Ziegler polyethylene is advantageous and permits sterilisation. In the U.S.A. alone production capacity (mainly for use as plastic) was 10,000 tons in 1958, 60,000 tons in 1960, and was expected to reach 250,000 tons by the end of 1962. In the U.K. polypropylene is made at Wilton by I.C.I., present (1961) capacity is 11,000 tons per year and it will probably be trebled shortly. Courtaulds make it as sheeting and call it "Propylex". At Wilton, pilot-plant quantities of fibre are being produced, and it should soon go into big production. Montecatini, by far the biggest Italian chemical company, makes the fibre at Milan and calls it Meraklon; 1960 production was 5,000 tons, output for 1961 being 10,000 tons; in America under the name Novmont they plan to build a fibre plant at Neal, West Virginia, which should produce 12,000 tons of fibre a year starting in 1962 or 1963. Japan made 35,000 tons in 1968. There are great years ahead for polypropylene as a plastic and the immense capital investments now being made will find their reward. But as a fibre? For industrial purposes, yes. For tyres, the biggest single industrial use? Very doubtful with that low softening temperature, but undergoing intensive examination. For the home? Ironing temperature and dyeing are against it; possibly span-dyed for carpets, much less likely for apparel. Diverse uses for polypropylene have not always been as successful as they could have been. In 1972 the only polypropylene being marketed by I.C.I. Fibres was Spunstron. This is used exclusively for ropes which are to be seen everywhere at sea, from large cross-channel steamers to pleasure yachts.

The Split-Film Process

A major development for polypropylene was the introduction of the split (or slit) film process to its manufacture in 1964. Polypropylene is extruded as a film and this is stretched and split into flat filaments or narrow tapes. These can be simply twisted, which causes them to fibrillate and assume a round appearance. The properties of split fibres—strength, resistance to rot and chemical attack—are similar to those of polypropylene round fibres extruded

by conventional means, but the split-film fibres are 25 per cent cheaper to produce, and their production is easier and needs less highly skilled operatives. Often, the film is made from pigmented material to simulate natural fibres. The narrow flat ribbons can be woven directly (without being twisted), and a fabric made from flat warp and flat weft gives good cover, strength and resistance to microbiological and chemical attack. It can be, and is, used for the manufacture of sacking and of carpet backing.

Split-film polypropylene is becoming a dangerous rival to jute as a packing material; it is lighter, stronger, and has a much lower water absorption as well as its anti-rot properties. The political troubles of Pakistan have made the supply of jute irregular, whereas polypropylene can be made in unlimited quantities from oil refinery byproduct. The one trouble to which the split-film packages are prone is their slipperiness; sacks are required to be capable of being stacked without slipping. Most progress on split-film polypropylene has been made in the U.K., Japan and Germany. Polypropylene fibrillates more easily than polyethylene and is accordingly preferred for making a fibrous yarn by twisting a ribbon, but split polyethylene is itself useful for twines and ropes. Another advantage of the splitting process is that a small split-film plant can be operated economically whereas most man-made fibre operations, *e.g.*, chemical, polymerising and spinning, have to be done in giant plants if they are to be economically sound. An ordinary nylon or an ordinary polypropylene twine, if it is knotted, tends to slip, but the flat film which has been processed into a yarn is free from this annoying disadvantage. There is some trouble with degradation of the polypropylene in sunlight, and sometimes carbon black is added to the melt before spinning; this gives a black film and split film but one that is less prone to actinic degradation. There is also the fact that polypropylene is difficult to dye, but dyeing is not usually necessary for packaging materials; but sacks are often printed with the supplier's mark, and printing on polypropylene is not easy. The Asians who grow, harvest and sell jute will have to watch the position carefully, otherwise the world's carpets will be made without a jute backing; polypropylene backing is lighter and this facilitates carpet weaving, and moreover it does not absorb and so waste any dyestuff from the dye bath, when the carpet is dyed, as jute may do. Similar considerations apply to packing and baling materials. The day may come when considerable quantities of polyamide and polyester are similarly made from split film. One form of polyethylene that is made in Sweden has the descriptive name POLYSPILT.

Process. Mechanically the conversion *etc.* of film into fibres has opened up a novel field of invention. Three processes that have so far been either used or suggested are:

1. Barnag (Barmer Maschinenfabrik A. G. of West Germany). The polypropylene melt is spun, *i.e.*, extruded in the form of a tubular film which is first carried to the top of a cooling tower. When cool it is fed continuously to the drawing line where it is drawn (stretched) and split into individual tapes by fixed knives. It is run over a pinned roller which causes continuous splitting and fibrillation.

2. A similar process to that just outlined but using a bi-component film (also Barnag). When this is processed the two components shrink unequally, the layer with the highest shrink potential causing the other layer to contract and adopt a crimped formation which is considered advantageous; it improves the cover.

3. Shell have patented an embossing method. In effect, the film after extrusion and having being quenched with water is subjected to an embossing process, and the cross-section of the embossed film before it is stretched becomes as shown in Fig. 206. The embossing is done at a temperature below the



Fig. 206.—Cross-section of a polypropylene film embossed and ready for splitting.

crystalline melting point, doubtless to conserve strength. The film is stretched up to ten times its original length and breaks up into a multifilament-like material; *i.e.*, the fibrillation takes place during stretching and the stretched and fibrillated material is wound up continuously on a multiple bobbin reel. The product is found to be uniform. The process can be applied not only to the homopolymer but also to blends of polypropylene with polyethylene and even with polystyrene. It has been reported that for fine deniers (below six) conventional spinning is cheaper than film-splitting, but that for higher deniers the reverse is the case. For example, 15 denier split-film fibres cost 39p/kg. whereas spinneret-spun 15 denier filaments cost 47p/kg. Not too much attention should be paid to these particular figures, but the principle is sound; *i.e.*, film-splitting is economic on high deniers but not necessarily so on

low denier fine fibres. The outline of the process is shown diagrammatically in Fig. 207.

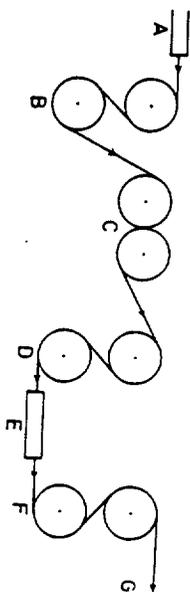


FIG. 207.—Diagrammatic arrangement of a split-film process.

- A. Extruder (spinning unit).
- B. Casting (the film) rollers.
- C. Embossing patterned (grooved) rollers.
- D. Arrangement of rollers to steady the speed of the yarn.
- E. Hot air oven in which the film is stretched to several times its original length.
- F. Arrangement of rollers to determine the speed of the yarn, and thereby the degree of stretch imparted to it. These rollers go several times as fast as rollers D.
- G. To winding creel containing many take-up bobbins or similar packages.

Production. In 1968–1969 output of polypropylene fibre exceeded 500 million lb. per annum. The main producing countries are:

U.S.A.	300 million lb.
U.K.	120 million lb.
Japan	50 million lb.
Italy	50 million lb.

TRILOBAL CROSS-SECTION FIBRE

Ordinarily, polypropylene fibres have cross-sections that are almost perfectly round. Melt-spun through a circular jet, just as nylon and Terylene are, polypropylene necessarily has, as they do, a round cross-section. Experimentally, polypropylene has been spun with a trilobal cross-section as described by du Pont in U.S. Patent 2,939,201 (1960). The molten polypropylene at 200° C. was extruded through spinnerets in which each hole was an equilateral triangle 9 mils long on each side and at each vertex of the triangle a square slot was cut running 3 mils in length from the vertex and being 3 mils wide. The yarn was wound up at 65 yards per minute and was hot-drawn at 124° C. to six times its length over a hot pin. Final tenacity was 4.6 grams per denier and elongation at break was 76 per cent. "The yarn of trilobal polypropylene filaments exhibited a unique luster highlight to the unaided eye, compared to the

dull flat appearance of the round filament yarn." It may not be long before all the melt spinners abandon round-section fibres; they have the lowest area/volume ratio.

Crystal Reality

As a rule, the crystals which compose a part (often a large part) of synthetic fibres are too small to be seen with a microscope; their presence is inferred from the behaviour of the fibre towards X-rays. It is doubtful too if discrete crystals usually form, more likely there are parts of the molecular assembly that are so orderly that they warrant the description crystalline.

But with polyethylene and isotactic polypropylene discrete crystals can actually be observed under the microscope.

Marker *et al.* have studied the crystallisation of polypropylene (m.p. 171° C.) at different temperatures. The progress of crystallisation was followed by microscopy: using crossed polarisers the amorphous layer of the polypropylene appeared uniformly dark, and crystals appeared first as small spots of light and gradually grew in circular patterns, forming beautiful spherulites nearly 1 mm. in diameter. Apparently the crystallisation is started by traces of foreign matter. All of the crystals start to grow within about 2 min. of solidification from the melt; after about 2 min. no new ones start but those already started continue to grow (the temperature being kept at about 130° C.) until after 8 hours they begin to touch each other.

Polypropylenes from different manufacturers behaved differently; the higher the molecular weight of an isotactic polymer the slower was the crystallisation and secondly the presence of some atactic (that is sterically irregular) polypropylene of high molecular weight in the nominally isotactic polymer slowed down crystallisation of the polymer.

The Vicat Softening Point

The Vicat Softening Point is often encountered in discussions on polyethylene and similar materials. It relates primarily to plastics and particularly to polyolefines. As these are fibre-forming materials the concept is useful to us, even although the actual test has to be made on a massive specimen and cannot be made on a fibre.

The Vicat Softening Point is defined (American Society for Testing Materials, *etc.*, A.S.T.M. Designation D1525/58T) as the temperature at which a flat-ended needle of 1 sq. mm. cross-section will penetrate a thermoplastic specimen to a depth of 1 mm. under a specified load (usually 1 kg. or 5 kg.).

Figures that come from different sources show some spread, but the following are typical.

	Vicat Softening Point (° C.) with	
	1 kg. load.	5 kg. load.
Old (low density) polyethylene	85-91	82-88
Ziegler polyethylene	121-124	85-105
Isotactic polypropylene	130-145	

It is of interest to us that the softening point (Vicat) of polypropylene varies with the degree of isotacticity, the greater the tacticity the higher the softening point as the following figures illustrate.

Isotactic index (per cent).	Vicat Softening Point at 5 kg. load (° C.).
77	72
81	74
85	78
90	86
95	98
97	106

Determination of the Vicat Softening Point is a very general method of test. It is not limited to polypropylene and has been introduced here only because it illustrates well the relation between thermal stability and tacticity of polypropylene.

POLYSTYRENE

Well known and extremely successful as a plastic material, polystyrene is a doubtful qualifier for inclusion in a book on fibres. It has been made as a flat monofilament, particularly by National Plastic Products Co. Inc., of Odenton, Maryland; its application was for use in knitted pot cleaners but it has been replaced by polypropylene.

The chemical structure of styrene or phenylethylene



is not very encouraging for conversion into a fibre-forming polymer, because most of the substance (the phenyl group) will constitute the side-chain and will not contribute to strength. Nevertheless, isotactic polystyrenes that have been made have had useful pro-

erties including a sharp melting point (220° C.) and good chemical resistance. Furthermore, the phenyl group offers a heaven-sent opportunity to organic chemists to introduce almost any desired functional group to give dye receptivity.

Perhaps some of the intensive research currently carried out on polypropylene may awaken interest in fibres from isotactic polystyrene, fibres that melt rather higher than nylon 6. Perhaps more likely, styrene will play the humbler part of co-monomer with propylene to make polypropylene dye receptive.

In 1965 Toyo Rayon Co. started to make polystyrene fibre at Hiroshima and contemplate a production of 30 m. lb. per annum.

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