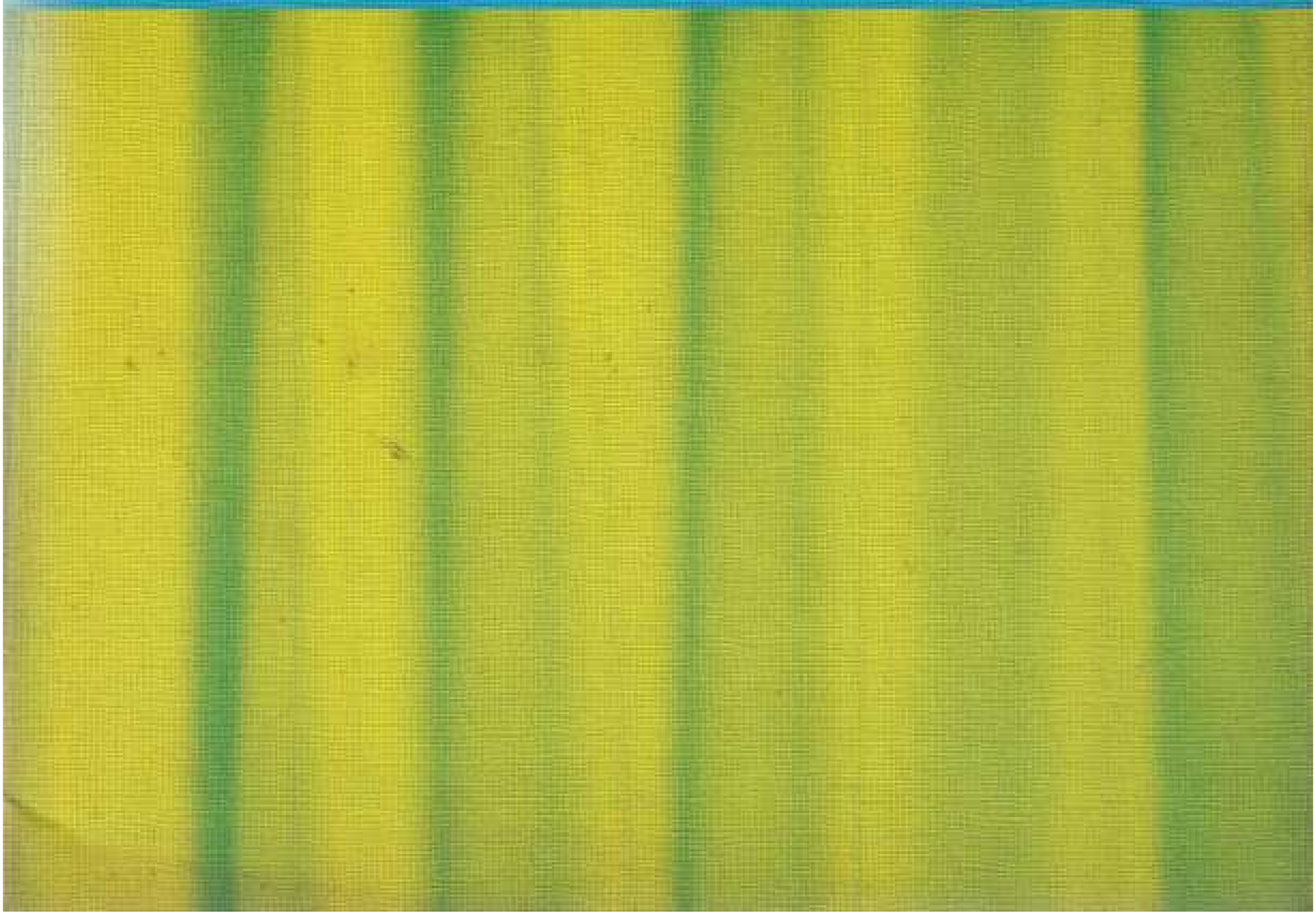
Chemistry Background Book

Man-made Fibres



'We are all Adam's children', said Thomas Fuller, 'But silk makes the difference.' Silk is a natural fibre that comes from unravelling the cocoon of the silkworm. It is thin and strong but expensive. The photograph shows a silkworm and a cluster of cocoons. *Radio Times Hulton Picture Library*

RS. 151

MAN-MADE FIBRES

In the Garden of Eden, Adam and Eve clothed themselves with fig leaves. Early man, living in harsh climates, wore animal skins. Then, so it is thought, people began collecting wool fibres, torn from the fleece of sheep by bushes and scrub. At first they probably pressed the fibres together to make felt. Certainly nomads in the Steppes of Russia and Central Asia have been making felts for thousands of years, and using them for tents and clothing. Then people learnt to spin the wool into a continuous yarn. In China they learnt to unravel the cocoon of the silkworm into a fine silk thread many hundreds of yards long. In India they discovered how to make another kind of thread from the seed hairs of the cotton plant and also sacking from jute. In Egypt they made linen from flax. Men relied on natural fibres and looked for fibres that were strong, supple and comfortable to wear.

Artificial silk – The idea that man might make fibres artificially, instead of gathering them ready-made from nature, came from observing the silkworm. To protect itself when it pupates, the silkworm forces out a liquid and the liquid hardens into a single thread on contact with air, enclosing the silkworm in a cocoon. In 1664 the English scientist Robert Hooke, who spent much of his time peering at things under the newly invented microscope, pondered deeply on this accomplishment of the silkworm. He thought that 'probably there might be a way found out to make an artificial glutinous composition much resembling, if not as good, nay better, than the excrement or whatever substance it be out of which the silkworm wiredraws his clew. If such a composition

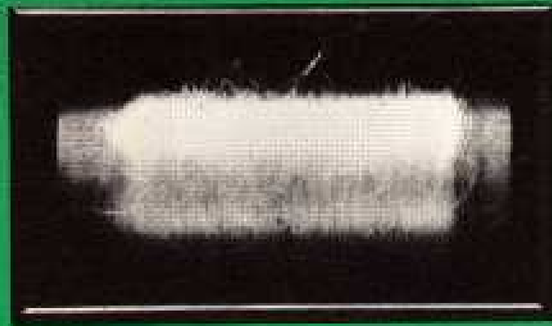
Count Hilaire de Chardonnet (1839–1924), who was the first to produce a man-made fibre on a commercial scale. The fibre was made from cellulose nitrate. Chardonnet called it 'artificial silk'.

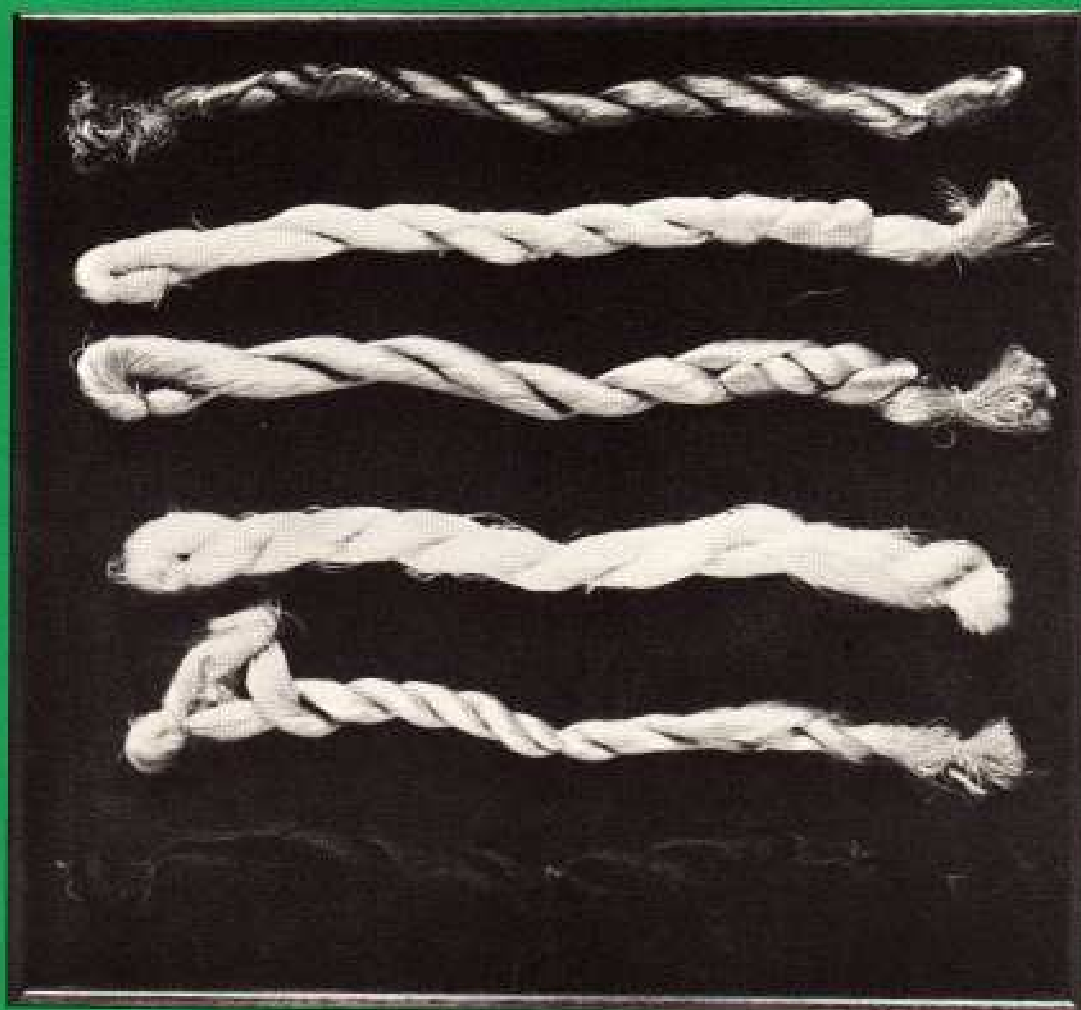
were found, it were certainly an easy matter to find very quick ways of drawing it out into small wires for use.' More than two centuries were to pass before Hooke's dream became a reality.

The first man to set about the manufacture on a large scale of an artificial fibre was a Frenchman called Count Hilaire de Chardonnet who worked for a time with Pasteur when he was investigating the silkworm disease. The substance that Chardonnet used was cellulose nitrate which also formed the basis of the first plastics, Parkesine and celluloid. Others before Chardonnet had tried to make threads from cellulose nitrate by drawing it out of solution with a needle. Chardonnet used what is called a spinneret which, in the way it works, imitates the spinneret in the silkworm and spider. The spinneret consists of a metal plate pricked with tiny holes. A molten substance forced (or extruded) through the holes emerges in the form of filaments.

Sir Joseph Swann in England was searching for a new material to make electric light filaments. He also tried cellulose compounds; but it was not until his daughters used the threads he made to crochet a few table mats that he realized it would be possible to make cloth with them.

Chardonnet opened a factory to make cellulose nitrate textiles in 1889 and, at the Paris Exhibition of the same year, he had fabrics on display under the name of 'artificial silk'. His textiles created a stir in the world of fashion, but unfortunately, when touched by a flame, they burned fiercely. Chardonnet eventually overcame the danger of fire by denitrating the cellulose nitrate and so producing a fibre of cellulose. But by then his





Specimens of artificial silk—the first successful man-made fibre. Its success was short-lived because fabrics made of it easily caught fire.

Crown Copyright
Science Museum, London

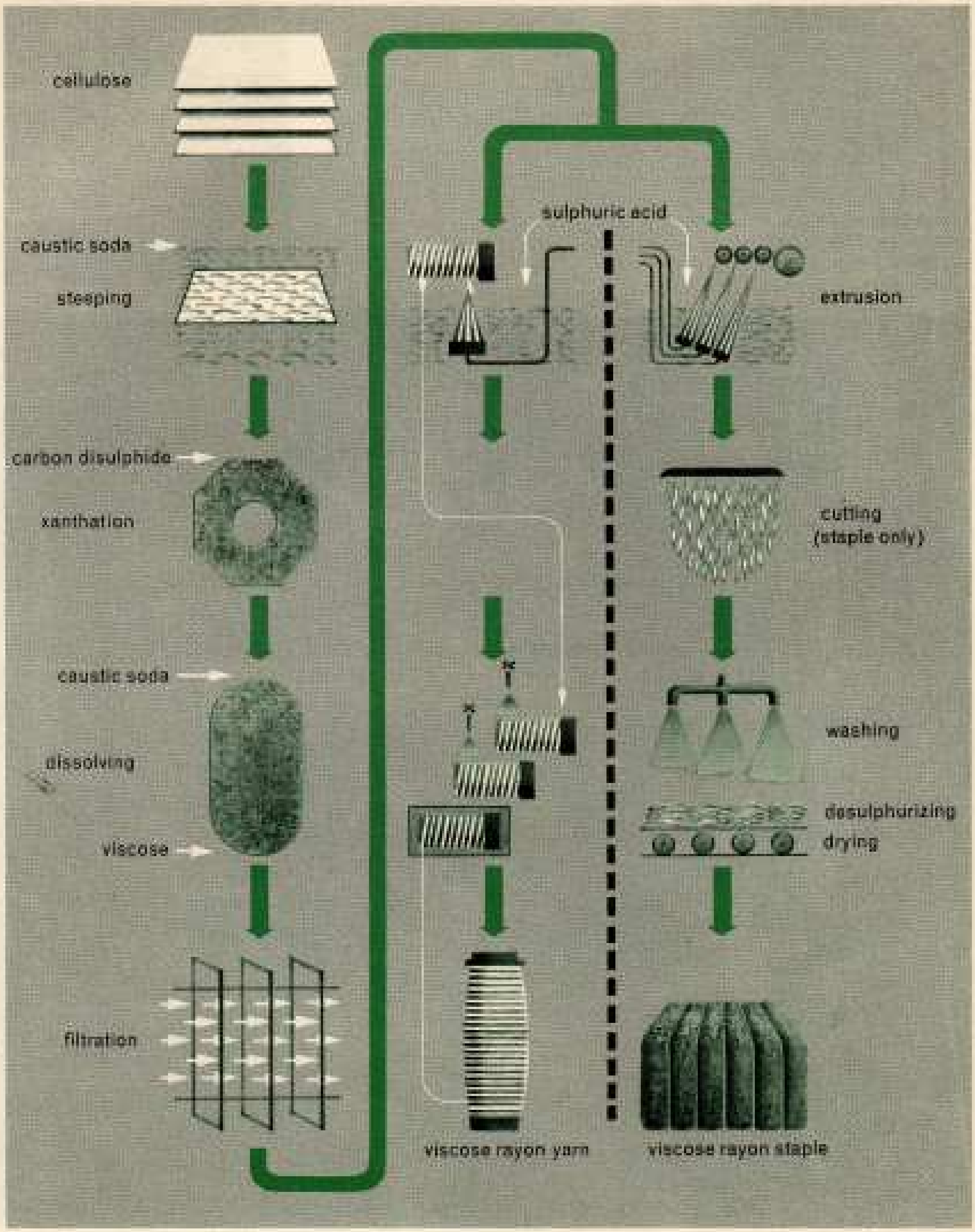
A bottle in which the first sample of viscose rayon was prepared – by the British chemists Cross and Bevan in 1892
Lent to the Science Museum, London, by Messrs Cross and Bevan of Lincolns Inn

process for making fibres was being challenged by others.

The first of these was the cuprammonium process in which cellulose is dissolved in an ammoniacal solution of copper hydroxide. The solution is forced through the holes of a spinneret into a stream of water. The filaments which form in the water are then passed through dilute sulphuric acid which gets rid of the 'cuprammonium'. By this process, filaments can be produced that are finer than silk, but nowadays the process is seldom used because it requires very pure cellulose. Thus, because of their several drawbacks, the first artificial silks and fibres did not have a startling success. The textile trade was not strongly affected until early in this century, when factories for making viscose were in production.

Viscose and acetate – The cellulose raw material used in the viscose process is wood pulp, which is cheap and readily available. The wood pulp is first immersed in strong caustic soda which disentangles the long-chain cellulose molecules. The alkali cellulose which results is then treated with carbon disulphide to form a crumbly yellow solid which, on dissolving in caustic soda, forms a syrupy orange liquid commonly known as 'viscose'. It is left to ripen for several days at scrupulously controlled temperature and humidity. The viscose is then extruded through a spinneret into a setting bath of sulphuric acid and metal sulphates. In the setting bath, the caustic soda is neutralized and the viscose, regenerated to pure cellulose, coagulates to form continuous filaments. Finally, the filaments are wound out

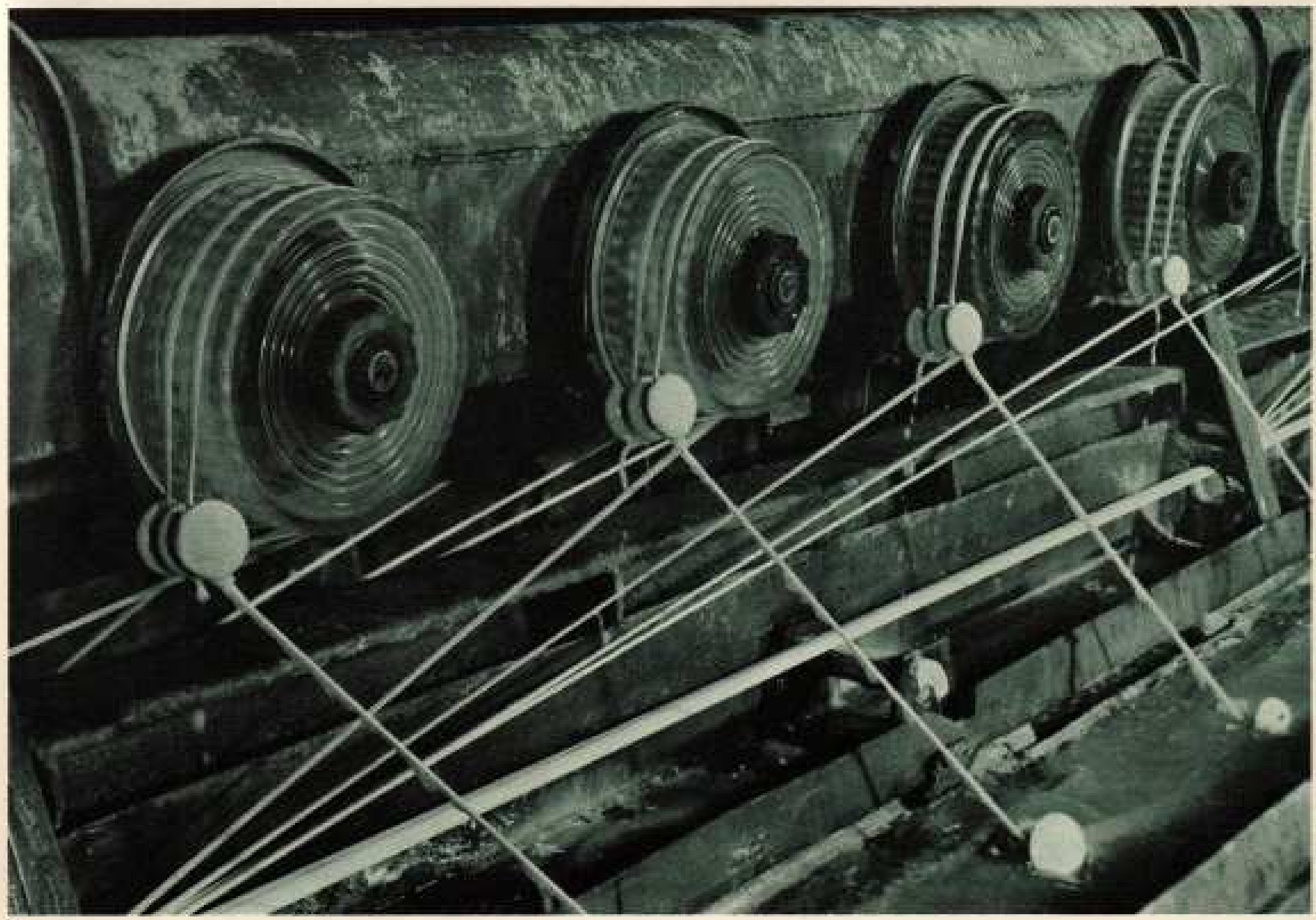
Flow sheet showing the manufacture of viscose rayon—both yarn and staple.



The starting point for the manufacture of viscose rayon is wood. Here spruce logs are entering a pulp mill. After several processes, the pulp will be transformed into rayon fabrics.
Courtaulds

Baling viscose rayon staple before it has been spun into a yarn. *Courtaulds*

Filaments of viscose rayon being wound out of the sulphuric acid bath during manufacture. *Courtaulds*



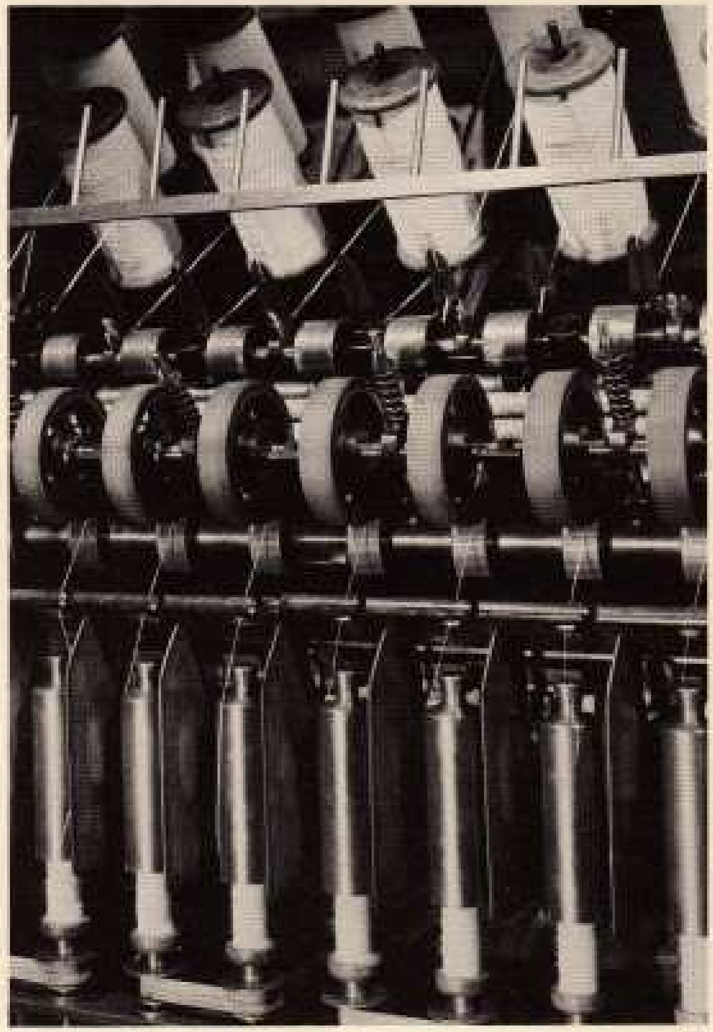
of the setting bath. Cellulose filaments made in this way become known as *viscose rayon*.

The next man-made fibre was *cellulose acetate*; this substance is not to be found in nature although its main component is still cellulose. Cellulose acetate was originally prepared by reacting acetic anhydride with cotton linters – the short hairs of very pure cellulose which remain attached to the cotton seed after the long hairs have been removed. Purified wood pulp is now generally used instead of cotton linters. To convert it into a textile filament, cellulose acetate is dissolved in acetone, and the solution is extruded through a spinneret into a current of warm air. The acetone evaporates, leaving filaments of cellulose acetate.

Viscose rayon was first used to make tassels, braids and knitted ties. Cellulose acetate, because it is not inflammable, was first used as a dope to coat the fabric of aircraft wings during the First World War. Afterwards, it was made into underwear and dress fabrics.

As people gained experience with these fibres, their properties were improved and their uses multiplied. Imitating the silkworm, scientists found it useful to stretch the filaments after they had been extruded. The stretched filaments were both thinner and stronger. At first the reason for this was not properly understood; but it was later made clear that fibres were formed of long-chain molecules. The increased strength of the filaments was caused by the re-alignment of the molecules to give a more crystalline structure. It was found that a variety of yarns could be made by cutting the continuous filament into short pieces from one to eight inches long (called staple) and then twisting them to-

Staple fibre—that is, raw wool or cotton or short lengths of man-made fibre—is spun into continuous yarns on machines such as this. The short fibres are on the vertical bobbins at the top and the continuous yarn is wound on to the bobbins at the bottom. The front set of rollers revolves faster than the back set and draws out the fibres into a yarn. At the same time, a twist is inserted to strengthen the yarn. *International Wool Secretariat*



A spinning room where cellulose acetate yarn is produced. The yarn is wound on to bobbins and stacked on metal racks. Like viscose rayon, cellulose acetate resembles silk and is used to make a variety of fabrics, especially dress fabrics. *Courtaulds*

The tyre-cord fabric in the wheels of this tractor are made of viscose rayon. So is most tyre-cord fabric. *Courtaulds*

In these machines, small chips of nylon polymer are melted and extruded through spinnerets to form filaments. Subsequently, the filaments are stretched to increase their strength. *British Nylon Spinners*

gether as in the traditional spinning of wool and cotton. From the staple, it is possible to produce yarns with a rugged texture that can be used in materials for suits, or yarns which are as fine as high-grade cotton.

Viscose and acetate, with their different affinities for dyes, also opened up new possibilities in the colouring of fabrics. For example, the cross-dyeing of a mixed fabric (say, cellulose acetate and cotton) produced an attractive effect of two colours. When this is done the fabric is described as 'shot', as in shot silk.

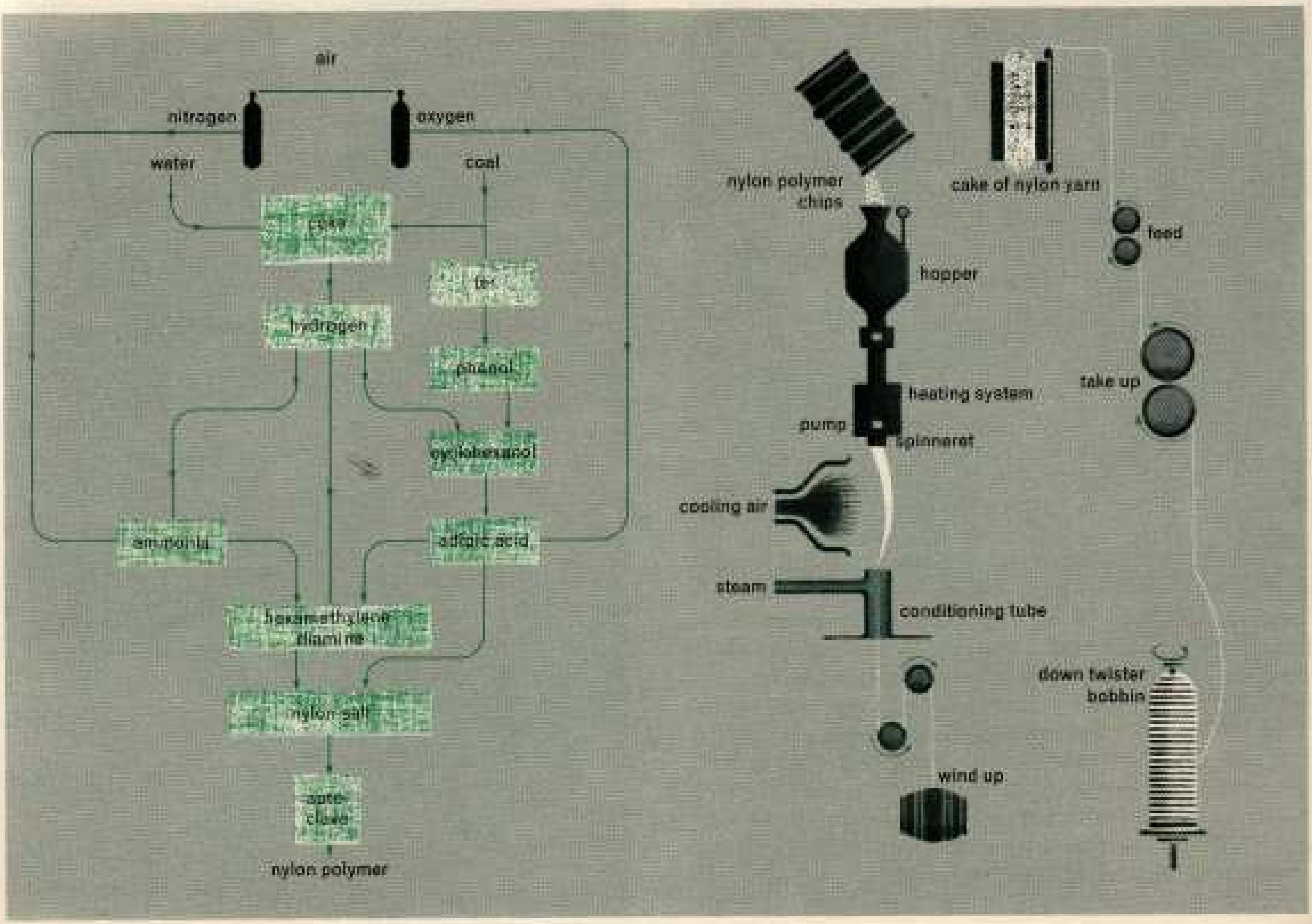
In a small way, viscose and acetate initiated a social change which the newer man-made fibres have perpetuated – clothing is no longer an obvious means of distinction between rich and poor. At the time that these fibres were introduced, the first big stores were starting business. Changes in fashion came about more rapidly because these stores were able to copy cheaply the costly clothes of the fashion houses. Silk and satin had always been very expensive and dresses made from these materials had been made to last for a long time. Cellulose fibres are much cheaper and, as women became accustomed to buying new clothes more often, new fashions were much easier and cheaper to follow. Another factor in this trend was the increasing freedom women had won for themselves. As they went out to work, they had more money to spend on themselves. Because they led more active lives, their skirts were made shorter. One consequence of this was that they had to pay more attention to their stockings, which were now visible. It was the introduction first of viscose rayon, and then of nylon, displacing silk, which made possible the manufacture of smart and cheap stockings.

A dress made from tricellulose acetate. This fibre has some of the useful properties of such completely synthetic fibres as nylon and Terylene: it dries quickly and resists creasing. *Courtaulds*

A light-weight sweater made of viscose rayon. This man-made fibre, which resembles silk, was the first to have a really big impact on the clothing trade. Since its appearance at the beginning of the century, various ways have been found to improve its texture and to increase its strength, especially its wet strength. It is now manufactured in larger tonnages than ever before and, as well as clothing, it is used to make a number of other textiles such as carpets. *Courtaulds*

Flow sheet showing the manufacture of nylon polymer and nylon yarn. Petroleum is sometimes used instead of coal as one of the raw materials of manufacture.

Weaving a fabric from a cellulose acetate yarn. The weaving machine is called a loom. The parallel vertical threads are called the warp. A shuttle moves rapidly backwards and forwards across the loom carrying a transverse thread called the weft. *Courtaulds*



Moreover the cellulose fibres are not restricted to the manufacture of clothing textiles but are extensively used in industry. Most car tyre cords, for example, are made from viscose rayon.

To look at and to handle, the man-made cellulose fibres most closely resemble the protein fibre silk, but, because they are made either from cellulose or from cellulose derivatives, structurally they are much more like the natural cellulose fibre cotton. During the past thirty years, a number of different fibres have, in fact, been made from proteins – for example, from the animal protein 'casein' which is found in milk and also from the plant proteins in groundnuts. These fibres tend to resemble wool, but for various reasons – chiefly because they are not very strong – their uses are limited. For the next important advance we now turn to nylon and Terylene.

Nylon and Terylene – Nylon was not the first of the completely synthetic fibres – some German chemists had previously made fibres from polyvinyl chloride – but it was the first to reach the headlines. It resulted from the carefully planned research of Wallace H. Carothers, an American chemist of extraordinary genius.

In 1927 the Du Pont Company of America launched a research programme to investigate, and possibly to synthesize, large molecules of the type found in such natural substances as rubber, cellulose and proteins. Carothers was put in charge of the research. Chemists of the time knew that the large molecules of these substances were made up from the linking together of much smaller molecular units – proteins from amino-acid molecules, cellulose from glucose molecules and rubber from isoprene molecules. Carothers's problem was how to make small molecular units link together to form larger molecules.

In his early work, Carothers investigated a number of polymerization reactions without thought of their practical applications. This soon led to the synthesis of *neoprene*, the first really practical synthetic rubber. Carothers then turned his attention to the possibility of synthesizing a textile fibre.

Attempts to synthesize natural fibrous materials – for

Dr W. H. Carothers (1896–1937), the discoverer of nylon. He also discovered neoprene, the first successful synthetic rubber, and is shown here stretching a piece of it. *Du Pont*

example, cellulose from glucose or proteins from amino acids – had proved abortive. Indeed, no one has yet managed to synthesize these complex materials. Working like an architect, except that his building bricks were molecules, Carothers began to design the types of very large molecule that he thought he could make, and here he directed his attention to the then little explored field of condensation polymers (see the Background Book, *Plastics*). Of the many polymers that he and his research team made, the most promising ones appeared to be polyesters – products resulting from the condensation reaction between dicarboxylic acids and dialcohols. When cooled, polyester fibres could be drawn out to several times their original length into filaments that were extremely strong. The trouble was that they could not be made into cloth because they dissolved too easily in water.

Carothers extended his investigations, using diamines instead of dialcohols. On 28 February 1935 he synthesized the first polymer from adipic acid and hexamethylene diamine. The general equation for this reaction is as follows:

$$nH_2N(CH_2)_6NH_2 + n\ HOOC(CH_2)_4COOH \longrightarrow$$

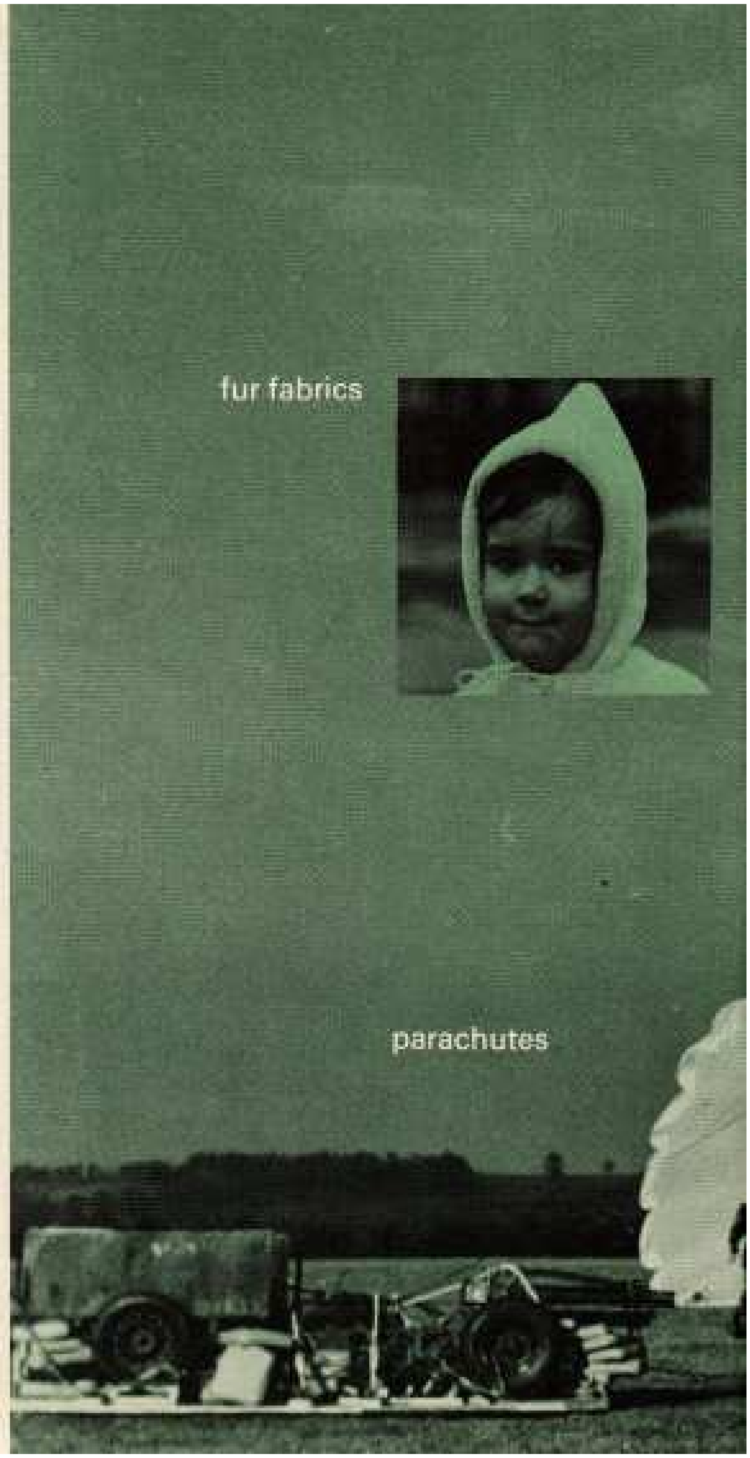
$$n \ldots .\ HN(CH_2)_6\ NHOC(CH_2)_4CO \ldots .$$

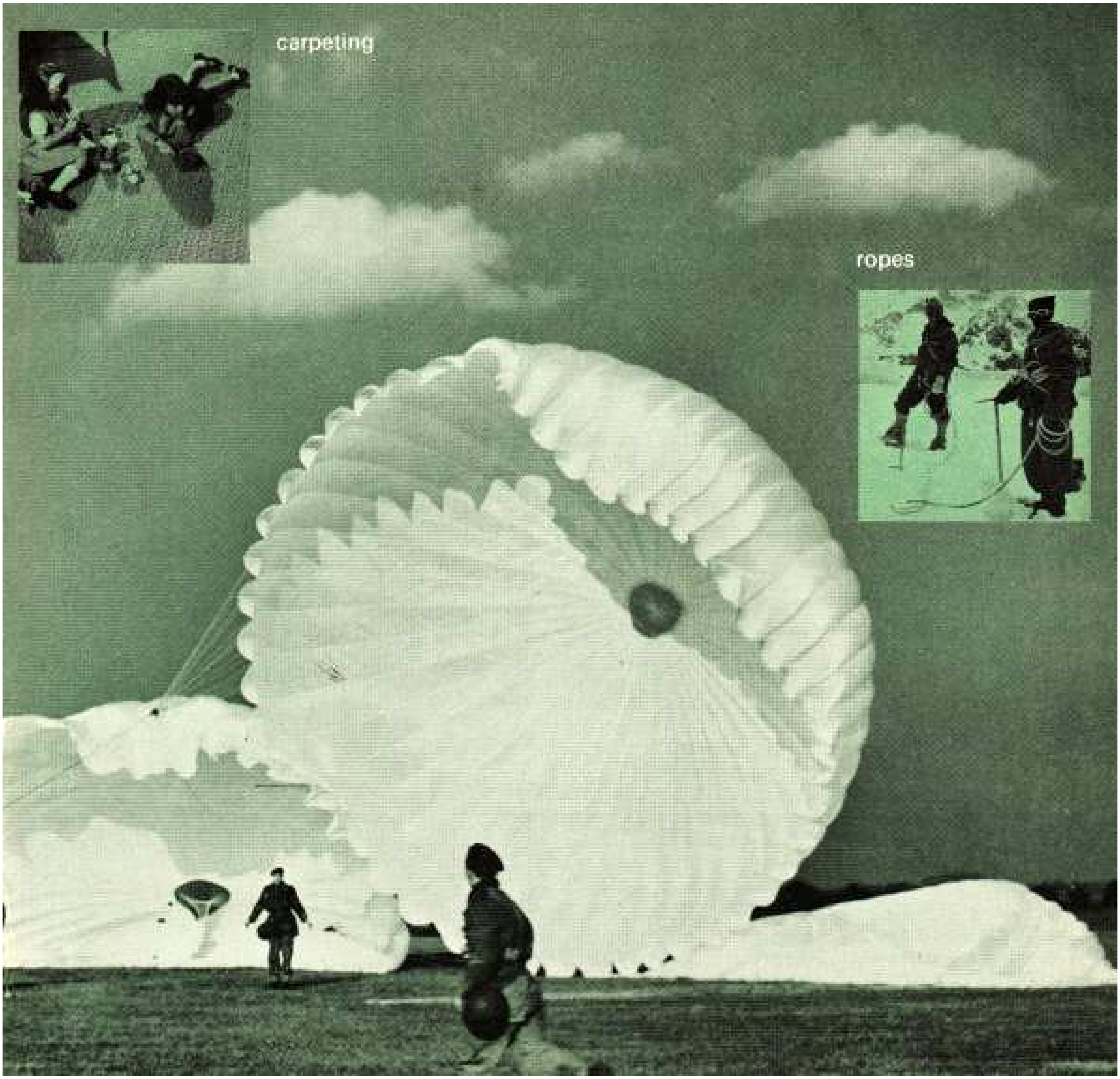
This polymer appeared to have many of the properties desirable in a textile fibre. It extended into filaments which, when stretched to several times their original

Nylon
One of the toughest and most versatile man-made fibres. It can be processed in many different ways to produce a variety of materials—as these photographs show.
British Nylon Spinners

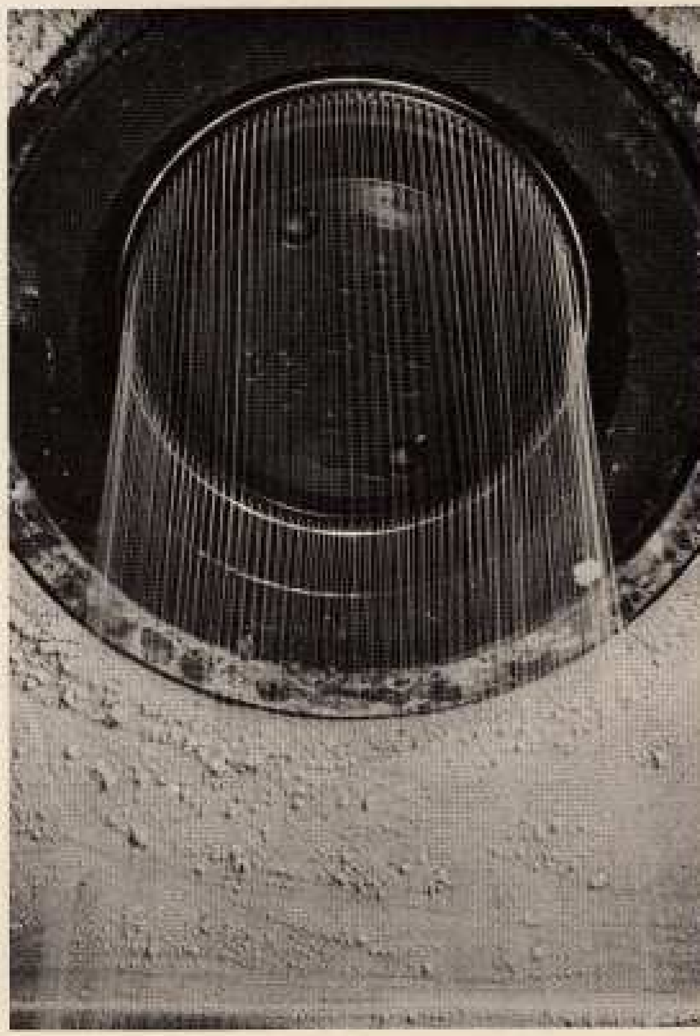
length, possessed many valuable qualities. They were extremely tough and hard-wearing. Unlike rayon, they were as strong when wet as when dry and they were more elastic than rayon. They were also mothproof, they dried quickly because they were relatively non-absorbent, and they could be set into permanent creases. Du Pont named the polymer 'nylon' and established a plant for the manufacture of nylon filament. Most of the raw materials were (and still are) derived either from coal or from petroleum.

At the 1939 New York World Fair stockings made from nylon were on display and immediately there was a great demand for them. However, it was not until after the Second World War that nylon became available in any quantity. Because of its special properties, many uses were quickly found for it. It replaced silk and viscose rayon for the making of stockings. It was used to make shirts and underwear. In its staple form, it was used to make socks and, blended with natural fibres, to make materials for suits. Fur fabrics, carpets, curtains, and a host of other textile goods made of nylon soon appeared. It was used to make many industrial fabrics. Its light weight and strength made it an excellent material for parachutes. Later, other polyamides—also known as nylon—were discovered and manufactured. Carothers's original discovery became known as nylon 66 because there are six carbon atoms in hexamethylene diamine and six carbon atoms in adipic acid. Newer types include nylon 610, made from hexamethylene diamine and sebacic acid (10 carbon atoms), and nylon 6 in which aminocaproic acid $(H_2N(CH_2)_5COOH)$ is condensed with itself. Nylon 6 was developed indepen-




carpeting
ropes

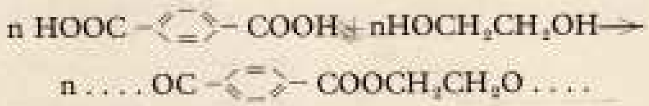
Molten filaments of Terylene emerging from a spinneret. Forcing substances through the small holes in a spinneret is the way in which all man-made fibres are produced. *I.C.I.*



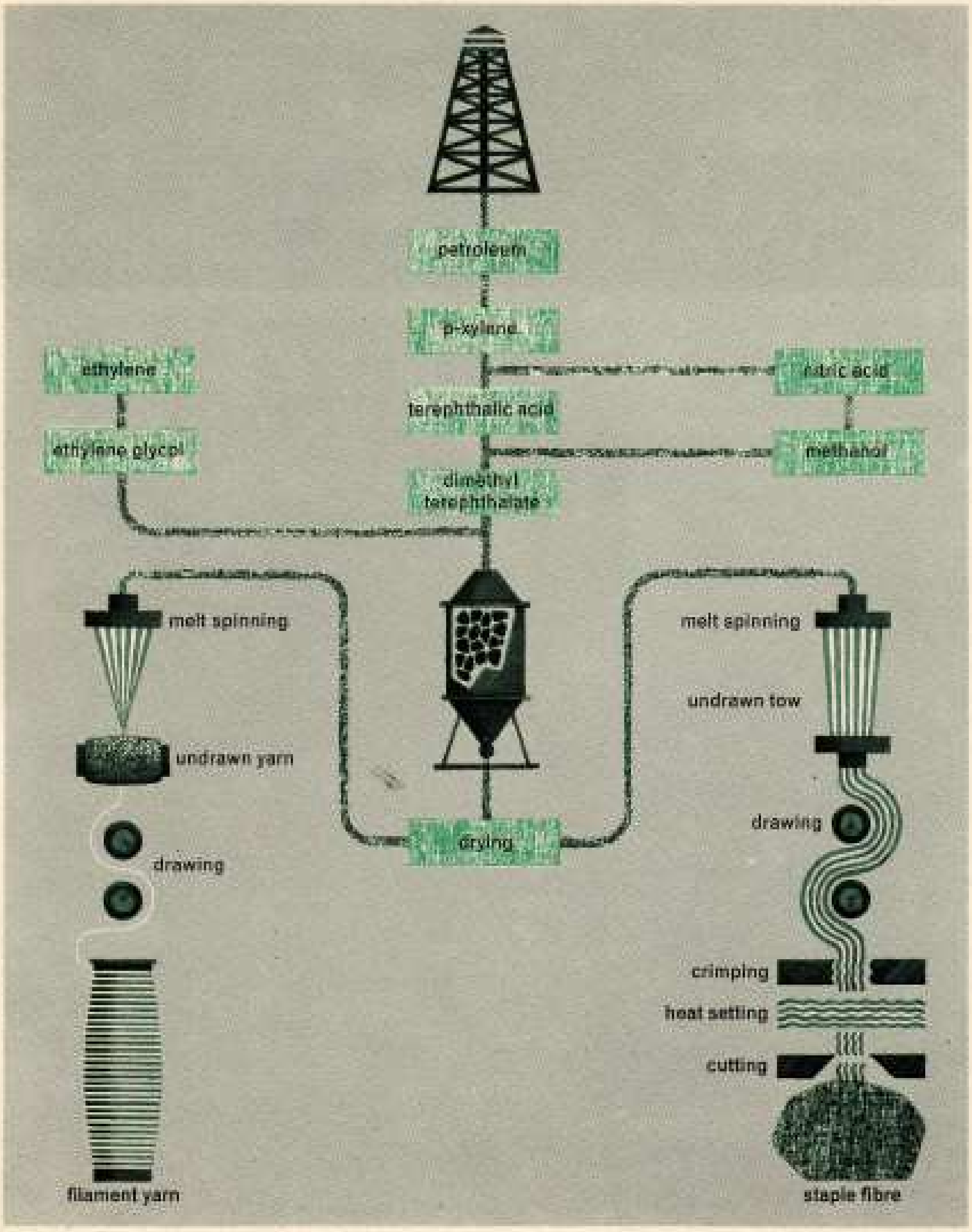
dently by German scientists during the Second World War when there was no exchange of information between Germany and America.

Another well-known synthetic fibre which appeared some years after the discovery of nylon was Terylene (known in the United States as Dacron). Terylene was discovered by two British chemists, J. R. Whinfield and J. T. Dickson, who at the time were working at the research laboratories of the Calico Printers Association Ltd., in Accrington, Lancashire.

Terylene is a polyester. Carothers had earlier investigated the fibrous possibilities of polyesters, but had not been lucky enough to happen upon Terylene. The Terylene polymer is made by reacting terephthalic acid with ethane–1, 2 diol (ethylene glycol).



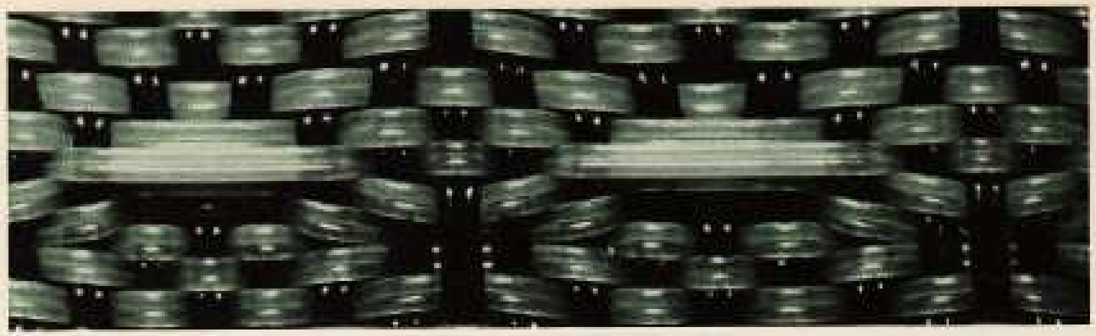
The stretched Terylene filaments have many useful properties in common with nylon, though the differences are enough to avoid duplication. On the one hand, Terylene has a texture more like wool–which is why it is more popular for suits, especially in blends with wool. Terylene also dries more quickly and, because it is little affected by sunlight, it is particularly suitable for curtain net. On the other hand, Terylene fabrics are slightly less hard-wearing, not so elastic (therefore Terylene is unsuitable for stockings), and less absorbent. The absorbency and texture of both nylon and Terylene can be improved by doing such things as 'crimping' the yarn to provide air spaces in the fabric.



Flow sheet showing the manufacture of Terylene polymer and of Terylene yarn and staple fibre.

A wide variety of clothes can be made from Terylene—as, for example, all the clothes this man is wearing, including his hat. It is an extremely popular material for suits, either on its own or blended with other fibres. It is also extensively used to make such things as fishing lines, tarpaulins, conveyor belts, and sails. *I.C.I.*

Close-up of a piece of patterned fabric made from polythene yarn. Such fabrics are very strong and are unaffected by most chemicals. They are often used to make industrial clothing. *Courtaulds*



Trawl nets made of polythene yarn. These nets are expensive and take a heavy battering from the sea. Making them from such tough fibres as polythene has greatly extended their useful lives. *Courtaulds*

World production of certain textile fibres

million lb. and per cent

Year	Man-made Fibres		Raw Cotton		Raw Wool		Raw Silk	Total
	M/lb.	%	M/lb.	%	M/lb.	%		
1959	6,812	21	22,622	69	3,222	10	72	32,728
1960	7,283	22	22,372	68	3,231	10	69	32,955
1961	7,749	23	22,004	67	3,277	10	70	33,100
1962	8,683	25	23,384	65	3,266	9	73	35,406
1963	9,685	26	24,019	65	3,326	9	69	37,099

Newer synthetic fibres – Other well-known synthetic fibres are Orlon, Acrilan and Courtelle. These fibres are made from polyacrylonitrile – produced by polymerizing acrylonitrile ($CH_2=CHCN$) – and differ from each other chiefly in added substances that affect the dyeing properties. All of them, in their staple form, have textures resembling wool of good quality. Teklan, a copolymer based on equal parts of acrylonitrile and vinylidene chloride ($CH_2=CCl_2$), is a fibre recently developed in Britain with a texture similar to silk.

Other fibres of importance are made from polyethylene and polypropylene which are much better known as plastics. Polyethylene has been developed mainly as a filament for ropes and twines and is used extensively in the manufacture of such things as trawl nets and deckchair covers. Polypropylene has recently been used to make blankets and (because it is resistant to both acids and alkalis) protective clothing for building and industrial workers. So far no one has invented a suitable method of dyeing these fibres; at present the molten polymer is coloured in bulk before it is extruded.

Polyurethane, also widely known as a plastics material, is now being used to make fibres with elastic properties superior to extruded rubber. Unlike rubber, the fibres can be dyed by conventional methods and do not perish.

Properties of fibres – The chemistry of synthetic fibres has much in common with that of plastics, as described in the Background Book, *Plastics*. Indeed, most of the newer polymers used to make fibres also have uses as plastics. Nylon, for example, is used to make gear-wheels and other machine components and Terylene is used to make adhesive tape and photographic film. However, not all plastics are suitable for making fibres. For conversion into a textile fibre, there are certain properties (outlined below) which a polymer should possess.

1. The chain molecules should be straight (not branched), and should not be less than 1,000 ångströms long.

2. The molecular units making up the chain should be arranged symmetrically and there should be no bulky side groups. In other words, the structure of the polymer should be highly crystalline. Drawing out the filaments after they have been extruded and so bringing the long-chain molecules into alignment, greatly increases the crystallinity of synthetic fibres.

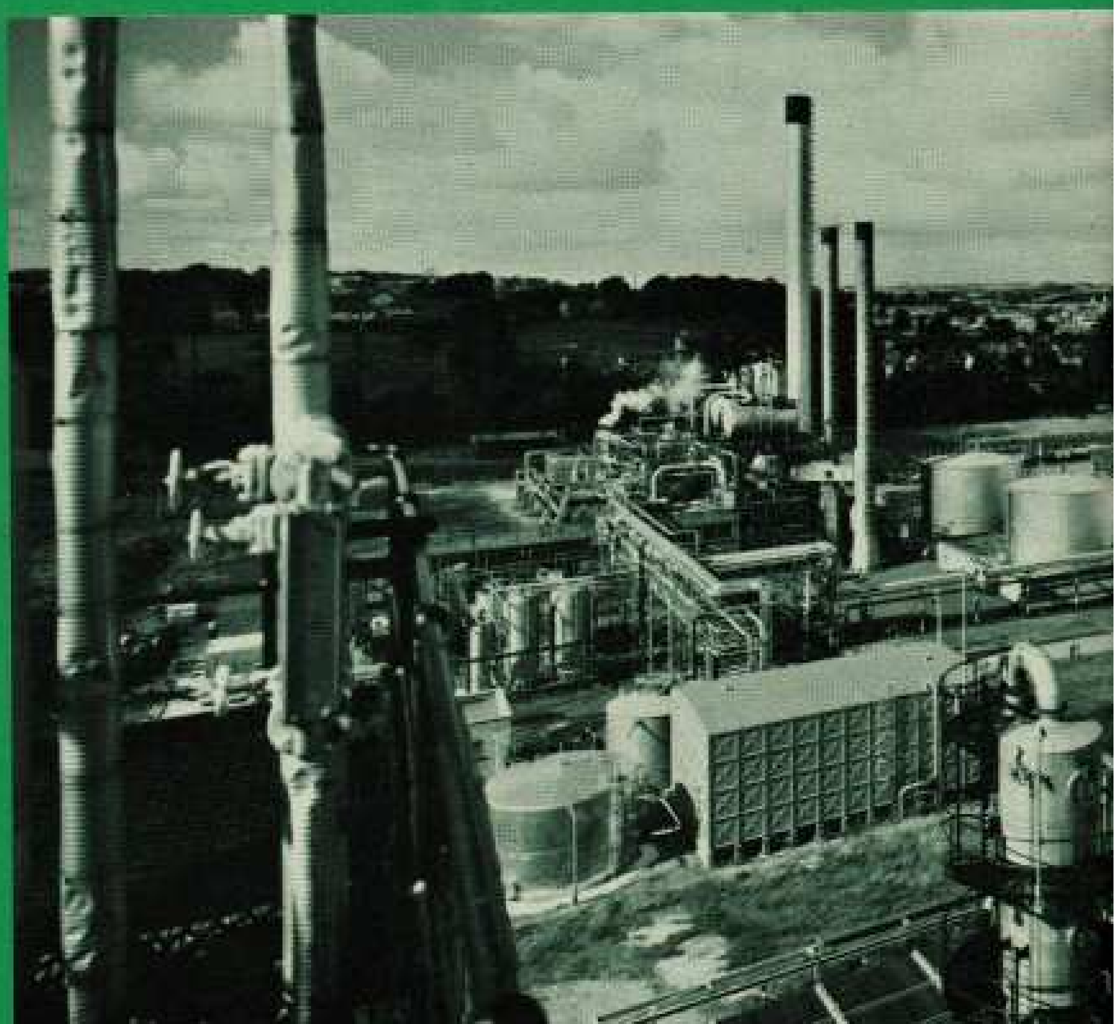
3. There should be evenly spaced polar groups in the molecular chains to give strong internal cohesion in the fibres.

As can be seen from the accompanying table, man-made fibres now account for a substantial part of textile production, and their use has affected a number of industries. Obviously this effect has been greatest in the clothing industry. Often textile machinery has had to be redesigned; spinning, knitting, or weaving techniques have been modified in order to make the fabrics. Here, a great advantage of staple fibre is that, whether it be viscose, nylon or any other man-made fibre, it can be spun on all types of textile machinery – either alone

Acrylonitrile (acrylic) fibres, cut into staple and spun into a yarn, have a texture similar to wool but are harder wearing. The three best-known acrylic fibres are Acrilan, Orlon and Courtelle.

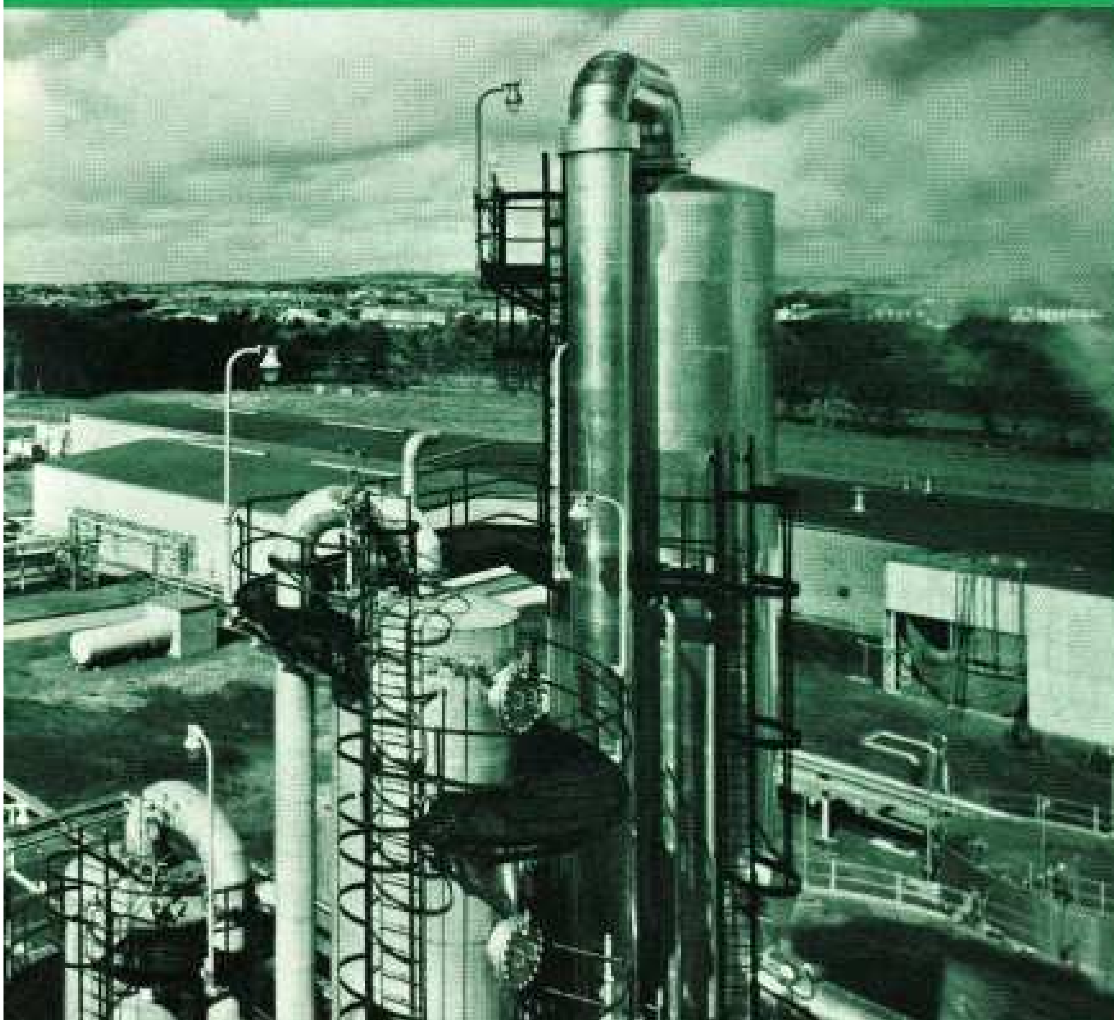
Factory for the manufacture of Acrilan—very different from the four-legged 'factory' in which wool is manufactured.
Chemstrand

Acrilan



Orlon

An Orlon sweater.
Du Pont



Courtelle

A coat and suit made of Courtelle
Courtaulds

Testing Terylene to find out how well it absorbs different dye stuffs. The chemical composition of a fibre largely determines its affinity for a dye. Man-made fibres often require new dyes and new methods of dyeing. Using a mixture of fibres with different affinities for dyes, it is possible to produce fabrics with a wide range of colour effects. *I.C.I.*

or blended with natural fibres. Yarn spun on cotton-spinning machinery tends to resemble cotton; yarn spun on wool-spinning machinery to resemble wool; and yarn spun on flax-spinning machinery to resemble linen. Costs also come into it. When they are intended for cutting into staple, the filaments can be extruded in much greater quantity.

Because nearly all the man-made fibres are strong, crease-resistant and are not attacked by moth, they have presented a challenge to manufacturers using natural fibres. Consequently there have been great efforts to improve the properties of natural fibres. Wool, for example, is often made moth-proof, and techniques have been devised for putting permanent creases into woollen fabrics. Other industries that have been affected by man-made fibres are the dyeing and dry-cleaning trades. Fabrics made from synthetic fibres are relatively non-absorbent and therefore they have to be dyed and finished by new and complex processes. To clean them new solvents have had to be found. The housewife, too, has to be careful about washing and ironing because fabrics can be damaged by too high a temperature.

As to the future, other man-made fibres will doubtless appear as chemists produce more new substances suitable for fibre manufacture. In the meantime, the present man-made fibres, either on their own or blended with others, offer a host of possibilities. Certainly the chemist has dramatically changed the clothing industry from what it was fifty years ago.

Questions

1. Make a list of articles of clothing that are made from the following fibres:

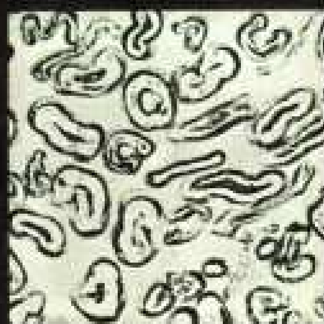
a. Viscose rayon.
b. Nylon.
c. Terylene.
d. Orlon.

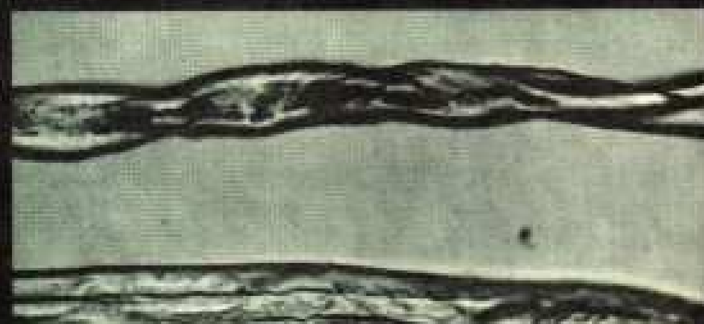
2. What are some of the advantages and disadvantages of man-made fibres compared with natural fibres?

Some fibres under the microscope – both in longitudinal section and in cross-section. Fibres may be produced in a variety of thicknesses. The term 'denier' – which is the weight in grams of 9,000 metres of the fibre – is used to indicate the thickness. The lower the denier, the thinner the fibre.

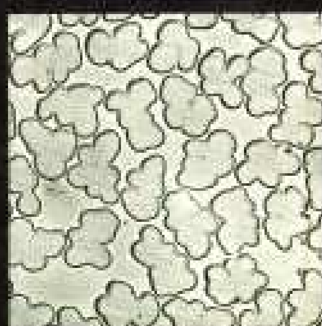
Cross section | Longitudinal section

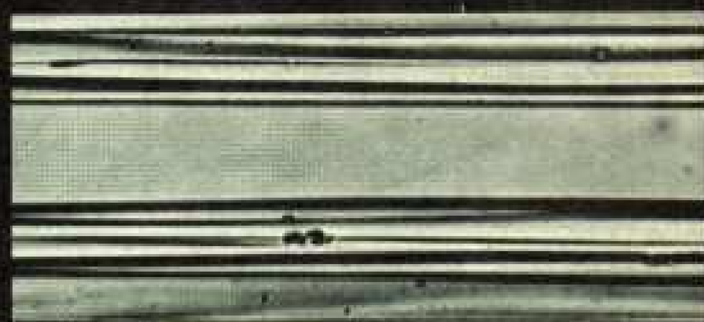
cotton



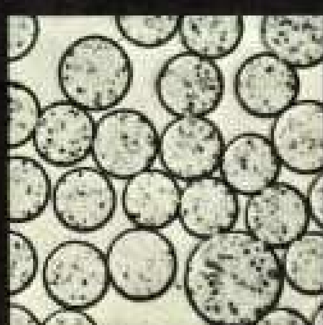


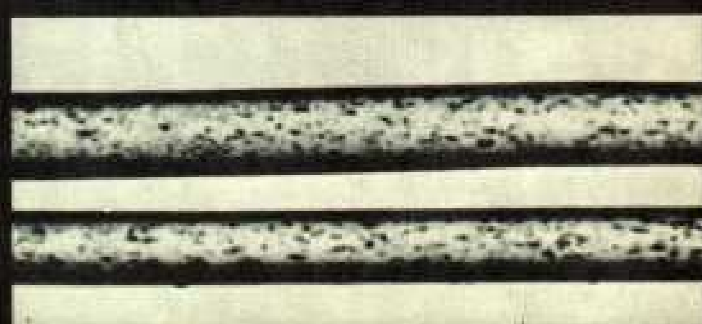
cellulose acetate





Nylon





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