MAN-MADE FIBERS HISTORY

Artificial cellulose fibers

The first man-made fibers which were developed and produced used polymers of natural origin, more precisely of cellulose which is a raw material available in large quantities in the vegetable world.

The beginning of industrial production of man-made fibers goes back to the year 1890, when the French Count Hilaire de Chardonnet started up his plant for the production of “Chardonnet silk” (initial output: 50 kg per day), using the cellulose nitrate process.

As it happens in general in the case of technical-scientific developments, this achievement was the result of previous studies and researches (since approximately the year 1840) focused mainly on the chemical properties of cellulose.

In particular the researchers found the way to treat cellulose (a material insoluble in usual solvents and inflammable) with nitric acid (nitrification), to dissolve the derivative with solutions of alcohol-ether, to prepare suitable extrusion devices (spinnerets) and finally to regenerate cellulose through saponification in alkaline baths (denitrification) in order to eliminate the danger inherent in the nitro compound (inflammable and explosive). Actually the birth date of the “artificial silk” (such was the name given to this fibre at its introduction) is said to date back some years before (1884) when an Englishman, Mr Swan, produced small quantities of nitrocellulose which the researcher had in mind to user the development of incandescent bulbs.

More or less in the same period another way had been searched for to make cellulose capable of being spun, after being discovered that cellulose could be dissolved in a mixture of copper oxide and ammonia (Schweitzer’s reagent, 1857). In fact this principle had been the basis in Germany for the production initially of incandescent bulbs (1891), then of cuprammonium fibers (1897) via the so-called “cupro” process, which was improved with the draw-spinning process (1891) and resulted in the production of Bemberg cupro yarn in 1909.

Meanwhile a patent had been registered in England by the researchers Cross, Bevan and Beadle (1892) for the production of sodium cellulose xanthate and for its dissolution in dilute caustic soda. In this way the basis were laid for the production of a man-made cellulose fibre, now called viscose, which remained for decades the main process in use for the production of manmade fibers.

The first industrial plants were built some years later in England and in Germany (early 1900), and contributed to the rapid decline and giving up of the Chardonnet process (which was left off in Germany in 1911).

One of the various chemical properties of cellulose which found particular interest was the possibility of esterificating with acetic acid the three hydroxylic groups contained in the glycosidic group of cellulose; the first product to be obtained was triacetate (1894) which, as it was later on discovered, could be partially hydrolized (1905) into a product which was easily soluble in acetone.

However only later on the most was made of the capacity of cellulose acetates to be transformed into fibers; the fibre which attained more relevance was cellulose diacetate (1919-1921), commonly named acetate, whereas triacetate (produced since 1914) found limited commercial interest owing to its difficult dissolution, restricted only to chloroform. Cellulose fibers were produced with said processes in form of continuous filament yarns, as the primary objective of the researchers was the reproduction of the morphology and, at least 7 partially, of the properties of raw silk (from which the term “artificial silk” originated). In 1920 the fibre was made available also in form of staple fibre (“Vistra”, Germany) and as such attained in time relevant market importance.

Recent years saw the development of a process for the production of cellulose fibers using a solvent specifically studied for cellulose (N-methylmorpholine-N-oxide), which on one hand safeguarded to a greater extent the inherent properties of the original cellulose structure and on he other permitted the use of processes less polluting than traditional ones. In this connection we cannot but emphasize the role played by the Italian industry within the sector of cellulose fibers.

The first factories sprang up at the beginning of last century thanks to the initiative of French chemical groups and in 1914 could supply 150 tons of rayon (this was the name given to the ontinuous filament fibre).

The first post-war period saw the successful coming on stage of the company SNIA which, through the concentration of various production units, became at the end of the 20’s one of the major world producers of viscose rayon and later on of viscose staple fibre. In 1927 the production of cuprammonium yarn was started on behalf of the company “Seta Bemberg S.A.”. In short, the Italian production rose from 320 tons in 1919 to 32,500 tons in 1929, so that Italy became the leading producer in Europe with a 16% share of world production. At the outbreak of the 2nd World War the Italian production had reached 120,000 tons.

The post-war period recorded a recovery of this industry, which reached its peak with 226,000 tons in 1964; from that date on, at first slowly and later at a quick pace, artificial fibers made room for synthetic fibers. As regards artificial fibers, it needs to be reminded that this group of fibers includes also fibers which have as raw materials natural polymers other than cellulose, like fibers derived from proteins.

A considerable historical significance was attained in Italy by protein fibers derived from casein, which were produced initially by SNIA in 1936 (researcher: Ferretti) under the name Lanital, later on renamed into Merinova.

Protein fibers of animal origin (casein from milk) stopped to have commercial significance, whereas still to-day a certain interest is enjoyed, especially in the USA, by protein fibers of vegetable origin (maize, peanuts).

Synthetic fibers

The development and production of synthetic fibers (obtained by synthesis of chemical compounds) are a rather recent achievement. The delay in developing these fibers is to be ascribed to an insufficient knowledge of the structure of natural polymers (such as cellulose, rubber, natural fibers), which were difficult to be studied from the chemical point of view because they were nor fusible, nor reactive and not even soluble: in short, they were completely different from usual chemical substances.

The basic studies carried out in the 1920's by Staudinger, a German researcher, brought out the fact that natural polymers are formed by linear macromolecules, that is by long thread-like chains, reproducible through the reaction of suitable, relatively simple molecules. Even if the date of birth of synthetic fibers is traced back to the production in 1931 of a chlorovinyl fibre (PE-CE, Germany), the fact is that the first real synthetic fibre in industrial production which would have a heavy impact on the market was the polyamide fibre, launched by the company DuPont under the trade-name "nylon" (experimental production in 1938).

The fibre came to success when the researchers obtained a product (polymerised amide, from which the name polyamide) by condensation of molecules presenting two reactive aminic groups (hexamethylenediamine) with molecules characterised by two carboxylic reactive groups (adipic acid).

In order to be differentiated from other polymers belonging to same chemical class, this polymer was marked with the acronym 6.6 which indicates the number of carbon atoms (that is 6) in the two molecules forming the repetitive polymer unit.

In that same period (1939), as a result of researches carried out in Germany by Mr Schlack in 1938, starting from caprolactam, a single molecule of basic monomer, a new polyamide fibre was produced under the name "Perlon" (type 6).

In those years, starting from terephthalic acid and glycol ethylene, polyester fibre was invented (Whinfield and Dickson, Great Britain, 1941) along with acrylic fibre (German and American patents, 1942); owing to war vicissitudes, the industrial plants were however started up only in the early 50's.

It is quite remarkable that in so few years all man-made fibers of primary importance for the textile sector (polyester, polyamide and acrylic fibers) were developed. Only later on an Italian researcher, the Italian Nobel prize Giulio Natta, discovered the possibility of synthesizing polypropylene according to a principle of structural regularity (1954), thus laying the basis for the production of polypropylene fibre (1959).

This survey on man-made fibers was recently integrated by some fibers of considerable importance, introduced into the market by the company DuPont: the elastane fibre “Lycra” in 1959 and the aramidic fibre “Nomex” in 1962.

On the scenario of synthetic fibre production, Italy made its appearance in 1939 with the production of small quantities of nylon (company Montecatini). The war blocked every development, but the production of polyamide fibers started up again in the post-war period, to reach 7,500 tons in 1956.

In 1955 the company Rhodiatoce started the production of polyester fibers under the name “Terital”; in 1959 the Edison group produced the acrylic fibre named “Leacril”, followed in 1961 by the industrial production of the polypropylene fibre named “Meraklon”.

The producers of man-made fibers renewed in the 60’s the great effort made by the producers of artificial fibers in the 30’s, bringing in the years 1960-1970 the share of the Italian production on world production to about 5%.

However, starting from the years 70’s -80’s, a slow decline took place owing to lack of rationalisation of the production plants, to insufficient research and development activity, to overproduction, to the oil crisis and also to production delocalization from old-industrialised countries (Europe, USA, Japan) to the newly-industrialized countries of the Far-East (China, Taiwan, South Korea).

Source : ACIMIT Fondation