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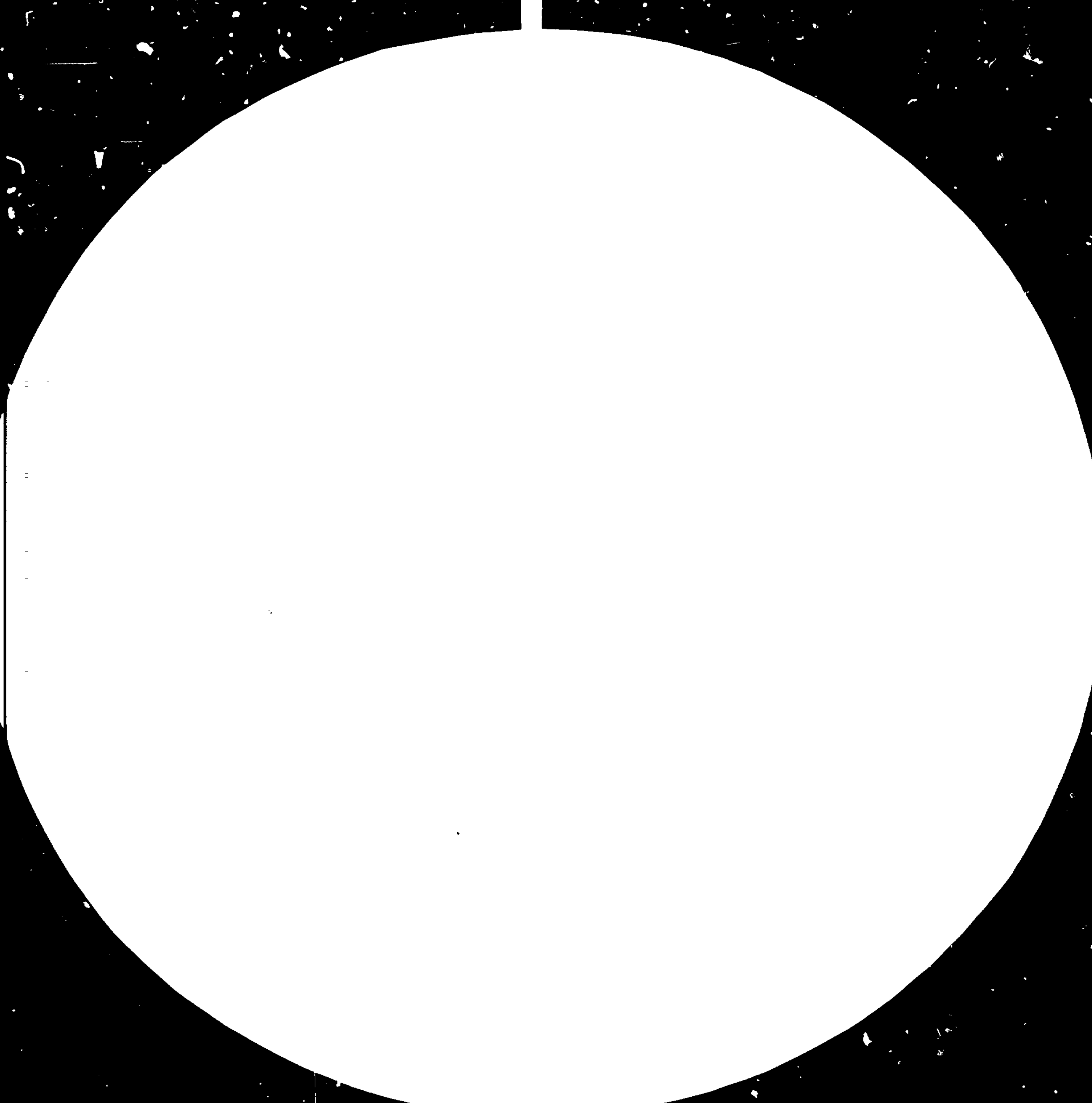
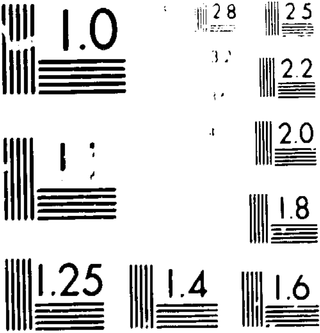




MICROCOPY RESOLUTION TEST CHART

09719 (I)

Man-made Fibers - Their Development and Economic Significance

by Dr. Hans Krässig, Director of Research and Development of Chemiefaser Lenzing AG

As far as our tradition and historical knowledge goes, we find that next to the concerns for food and shelter the concern for clothing has always played a major role in the development of mankind. Initially leaves and other parts of plants besides animal skins will probably have served to satisfy this need. Only later man has aquired the knowledge to spin threads or yarns from fibers obtained from plants or animal hair and to weave these threads or yarns into fabrics. According to historical findings woven material made from wool and fibers of hemp and of flax were known centuries before our times in what we call Europe today. Silk and cotton fabrics we owe to the Chinese, the East Indians and to the aborigines on the American Continent. Only in the course of the Middle Ages they were introduced on the European continent by way of the conquests of Arabs and Turks and as a consequence of the sea voyages of the Portugese and Spanish discoverers. In spite of this, wool has remained the most important textile raw material until far into the 18th Century and was only then replaced by cotton at a steadily increasing rate.

The idea to produce textile fibers by artificial means is still relatively young. The first proven statement of this kind

was made by the English scientist Robert Hooke, who in his book "Micrographia" says in 1665 the following:
"..... and I often thought that a process could be found to produce an artificial glue-like substance quite similar if not just as good or even better than the excretion or what other kind of substance it may be from which the silk worm spins its cocoon. Would it be possible to find such a substance it will certainly be easy to find very quickly also the means to draw from it useful filaments. I do not need to mention the usefulness of such an invention nor the profit which would accrue to the inventor."

Approximately 70 years later the French physicist and zoologist Rene Antoine Ferchauld de Reaumur wrote similarly in his work "Notes on the history of insects". In this connection he made a comparison with glass fibers which in his time were known but of little imprtance. Fibers from glass are such to be considered as the oldest artificial fiber material.

1. The development of synthetic fibers based on natural raw material:

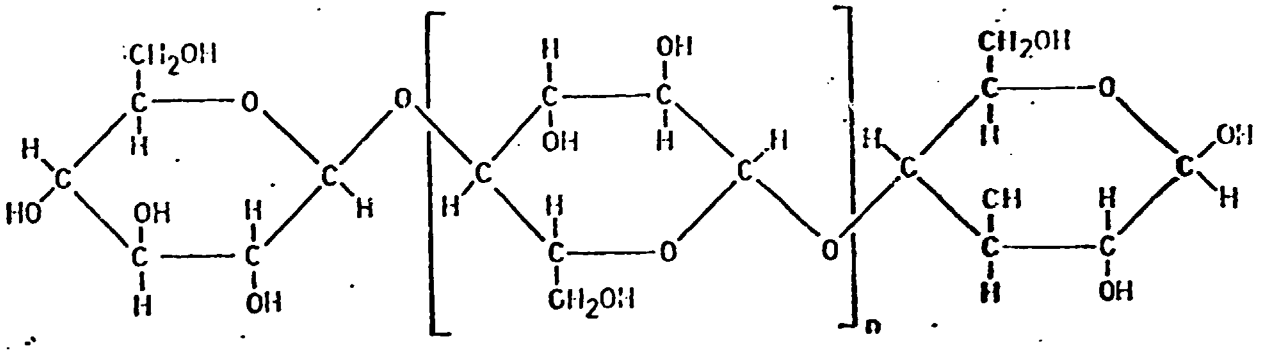
Until these thoughts could materialize almost 200 years had to pass. They did, however, introduce the second stage of development which is marked by the advance of chemistry into the area of making and processing textiles. It is interesting to note that not proteins, being the basis of silk or wool, furnished the raw material for the first and today still most important artificial fibers but cellulose. This may in part have been caused by the steadily increasing importance of the native cellulose fibers, especially of cotton. In part it may also be explained from the fact that the chemical and physical behaviour of protein solutions is much more complex because of the polyelectrolyte characteristics of the protein molecule than the behaviour of solutions of cellulose or cellulose derivatives. Various preparatory observations and developments advanced the development of the first artificial fibers proper.

The basis for the development of artificial cellulose fibers was the invention of processes to obtain the cellulose on a large scale from wood which was available on a large scale. Preparatory work for such processes began in the first half of the past century. It was Tilgman who in 1866 succeeded for the first time to do so on a technical scale through the use of sulphurous acid as means to pulp the wood. From this beginning the so called "sulfite-process" was developed which later was supplemented by the competing "sulfate-process".

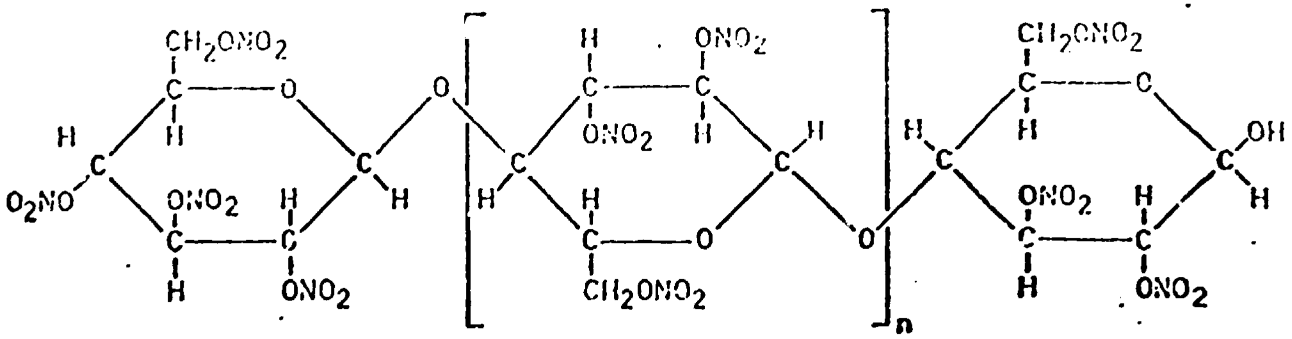
Furthermore, the finding of solvents for cellulose and of soluble cellulose derivatives was of basic importance. In 1832 Braconnot isolated the nitric acid ester of cellulose, which is soluble in acetone, as easily flammable material by the reaction of concentrated nitric acid with cellulose containing material. This ester obtained importance through the work of Schoenbein and Otto in the year 1846 and 1847 as so called "explosive cotton". Audemars showed in 1855 for the first time that it is possible to draw filaments from solutions of this material Of similarly fundamental character was also the observation by Schweizer in 1857 of the dissolving power of copper ammonia hydroxid for cellulose. It was the basis on which the Englishman Beston in 1882 made first experiments for the production of artificial fibers. Somewhat later the Englishmen Cross, Bevan and Beadle observed the formation of a water soluble derivative of cellulose in the reaction of cellulose with alkali and carbondisulfide. With the production of highly viscous cellulose and cellulose derivative solutions and with the observations that by pressing the solutions through small orifices and coagulating the extruding liquid filaments in coagulation baths or simply by evaporation of the solvent, in case of higher volatility of the solvent, the doors were opened for the production of artificial fibers.

It is interesting to note that the initial impulse for a systematic exploration of the problem of making artificial fibers in the 19th century was given by another eypochmaking invention, namely that of the electric light-bulb by Swan and Edison. The carbon filaments made from carbonized cotton were not satisfactory because of their irregularity. For this reason the manufacturers of electric light bulbs became interest in the possibilities for the production of more regular artificial carbonized filaments.

The oldest industrially used process for man-made fibers is based on the solubility of cellulose nitrate in organic solvents. Cellulosetrinitrate is made by esterification of cellulose with nitric acid in presence of esterification catalysts such as sulphuric acid. In this reaction the three reactive hydroxyl groups of cellulose are substituted by nitrate ester groups as this is shown in the following reaction scheme.



Cellulose



Cellulosetrinitrate

It must be mentioned, however, that the exact structure of the cellulose molecule and of the cellulose nitrate ester molecule was not yet known at that time. It was cleared up completely only in the twenties of this century.

Even though the first patent for the preparation of cellulose nitrate filaments was granted in 1855 to Audemars and another patent was granted in 1883 to the Englishman Swan for the denitration of such cellulosenitrate filaments with ammonium sulfide, this does not lessen the merit of the Frenchman Count Hilaire de Chardonnet with respect to the technical realization of the manufacture of artificial fibers by the nitrate process. He is actually to be regarded as the founder of the man-made fiber industry. To him we owe the technique of the wet and dry spinning processes of highly viscous solutions, for the conveying of which sizable pressures and correspondingly solidly constructed machinery and special conveying equipment were necessary. The successes of Count de Chardonnet have proven the correctness of the choosen ways. Even though, the cellulose nitrate fibers are hardly made anymore today their development was defining the right direction for the manufacturing processes for other man-made fibers on the basis of cellulose, which were developed later on.

Somewhat later the preparatory work of Despaissis, Fremery and Urban led to the development of a process for the manufacturing of artificial cellulose fibers by the so called copper ammonia method. In 1897 a basic patent was granted to

Hermann Pauly the claim of which reads as follows: "Process for the making of artificial silk consisting in extruding a solution of cellulose in copper hydroxide ammonia at low temperature through fine orifices into a liquid which decomposes the solution, for example acetic acid, whereby the filaments can be wound up, for example on a roll rotating in this liquid." The further development of this process which was carried out almost exclusively by German firms was advanced above all by the firm J. P. Bemberg AG, where Thiele in the year 1901 has given a further important impulse to the making of copper ammonia fibers of great fineness, which are still not superceded today, by the development of the draw spin process. Copper ammonium rayon, however, constitutes today only a small part of the total production of regenerated cellulose fibers.

Almost at the same time the English Courtaulds Ltd. in Coventry had started with the development of an artificial cellulose fiber working with observations of Cross, Bevan and Beadle on the water solubility of the sodium xanthogenate of cellulose.

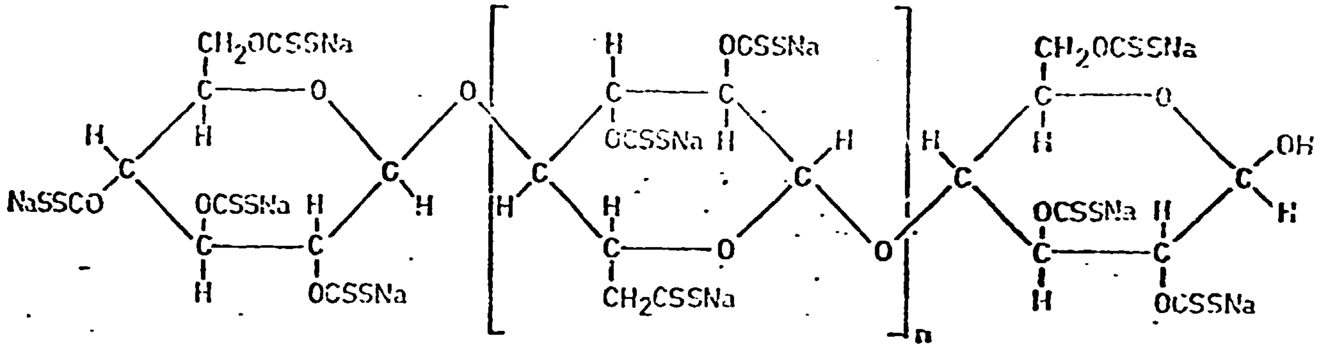
The cellulose xanthogenate is made by the reaction of cellulose, as for example wood pulp, with alkali and carbon disulfide, whereby the reactive hydroxyl groups of the cellulose are substituted with xanthogenate ester groups, as shown in the picture of its structure. (cf. page 9).

It must be mentioned here that during the technical or large scale xanthogenation only a small part of the hydroxyl groups is really reacting in this way.

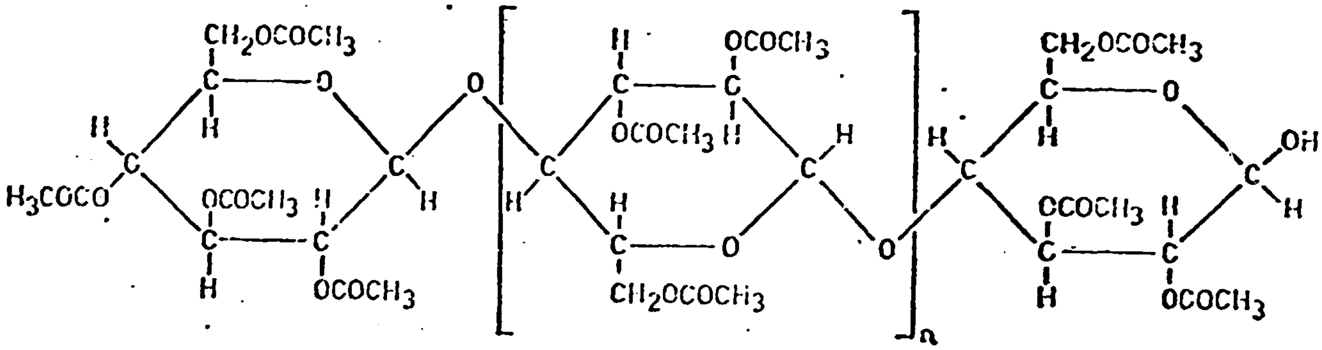
The actual break-through was achieved by Stearn who found that solutions of cellulose xanthogenate in alkali can be coagulated with solutions of ammonium salts. Because of the obvious success, also the German Vereinigte Glanzstoffabriken AG in Oberbruch near Aachen jouned into the development around 1905. In 1907 Müller found an excellent spinning bath consisting of a mixture of sulphuric acid and sulfates. The better economy of the viscose rayon process has made it the most important process for the production of regenerated cellulose fibers. Out of about 3,55 million (1977) tons, which constitute the world production of cellulose filaments and cellulose staple fibers, more than 80 % are made by the viscose-rayon process.

Beside these man-made regenerated cellulose fibers, the so called "acetate fiber" has gained importance. It was a long and difficult route from the first discovery of acetyl cellulose by Schützenberger in the year 1865 to the high level of production know-how of acetate fibers today.

Cellulose acetate is made by the reaction of cellulose with acetic acid anhydride in the presence of esterification catalysts such as sulphuric acid. In this reaction the reactive hydroxyl groups in the cellulose molecule are substituted by acetate ester groups as shown in the following picture of the structure of the molecule.



Cellulose trisodiumxanthate



Cellulose triacetate

In the year 1894 the Englishmen Cross and Bevan was granted a patent on cellulose acetate as a substitute for celluloide made from the easily flammable cellulose nitrate. However, the fact that the new product was not soluble in acetone and could not be gelatinized with camphor it was not used widely at first. The decisive advance was made in 1904 in America and in Germany at the same time. Miles on one hand, and Eigengrün and coworkers on the other hand, could show that by a partial responification of the cellulose triacetate a cellulose hydroxy acetate which is soluble in acetone is obtained. Hereby a way was found for the development of a manufacturing process for man-made fibers on the basis of cellulose acetate. The spinning of this fiber is carried out by the dry spinning process, which was developed already by Eigengrün in 1904 to a technical scale. Only because of the fact that initially there were hardly any dyestuffs available with which cellulose acetate could be fast-dyed, it was not before 1920 that this type of man-made fiber found a place beside the regenerated cellulose fibers. After these difficulties where overcome in 1920 by Clavel through the development of special dyestuffs for acetate fibers, the way was free for the further development of this fiber. The world production of acetate filaments and acetate fibers has risen within the last 35 years to approximately 550'000 tons. (1977)

The development of practically useful man-made fibers on the basis of protein has only started in the thirties. Although Millar has tried already in 1899 to make fibers from gelatine and Todtenhaupt has made man-made fibers from casein in 1904 according to his own patents, these were not accepted because of their unsatisfying properties. Only in 1935 the Todtenhaupt-process was improved by Ferretti to such a degree that his "Lana italiana" could be produced on a technical scale as "Lanital" and be brought onto the market. Man-made fibers made from protein were later fibers also produced in America from soya-bean protein and in England from peanut protein. All these man-made fibers, however, have not risen to any greater importance so far.

2. The development of man-made fibers based on synthetic raw material:

a) The importance of polymer science for synthetic fiber development:

While the man-made fibers described so far are made from native fiber forming raw materials, above all from cellulose materials, the morphological structure of which does not permit textile use without transformation processes, we understand under the term of"synthetic" fibers in the proper sense of the word fibrous materials made from products which are artificially made on the basis of products made from coal or from petroleum. Such products as for example polystyrene, polyvinylchloride, or polyvinylacetate had been known already for some time. Already in 1913 Klatte has made in a patent the proposal to produce fibrous materials from the latter two. This proposal, however, far advanced the state of science and technique of his time. Only in the course of the second decade after above all by the work of Hermann Staudinger the basic ideas of the macromolecular chemistry had been found, the full meaning of this pioneer patent was recognized by the industry.

Staudinger thus opened up the beginning of the third period in the development of textile fiber materials. Up to this time successes were largely the fruit of empirical and often disappointing research activities, since the basic knowledge of the moleculare structure of fiber forming materials was still unexplained. Although, the composition of cellulose and proteines was known, hardly anything useful was known about the size and the shape of their molecules and their relations to the phenomenon of fiber formation and fiber properties. It is the merit of Hermann Staudinger to have expressed for the first time in 1920 the fact that within the molecules of fiber forming materials thousands and thousands of atoms are linked to form macromolecules according to the same principles as the teachings of structure by Kekule demand for normal organic compounds. In reactions under proper conditions it is possible to convert this materials into polymer analogue derivatives while retaining the macroradicals, as this has been practiced in preparative organic chemistry already for a long time in substituting atoms or groups of atoms on low molecular weight substances while retaining the carbon atom structure. In his famous model experiments with polyoxymethylene Staudinger was able to show, furthermore, that the fiber formation is a typical property of linear macromolecules. After Staudinger and his co-workers had been able in addition to that to clarify the relations between viscosity and molecular weight and partially also moleculare shape, the means had been found to characterize fiber materials whereby also the relations between fiber tenacity and molecular size could now be examined. With these methods the scientific tools were given to the man-made fiber industry with which research and development could be advanced systematically. It is not by chance that from then on the man-made fiber industry has developed so rapidly.

b) The importance of the knowledge on fiber "architecture":

Just as uncertain as the knowledge about the chemical structure of the molecules that make up the natural fibers were until 1920 the ideas of the "architecture" of fibers. The starting point of all newer theories about the morphological structure of fibers is the micellar theory developed by the Swiss biologist Naegeli more than a hundred years ago. His ideas are represented in Figure No. 1.

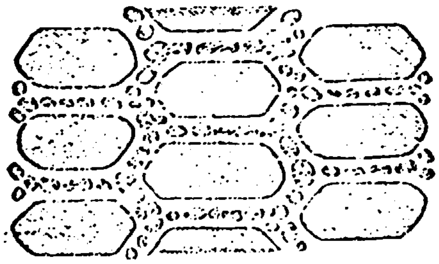


Fig. No. 1: Micellar structure according to Naegeli and Schwendener.

During the 1920's Naegelis ideas were confirmed by X-ray diffraction studies. The results indicated that in fibers there are defined cristalline regions embedded in an amorphous matrix. From such measurements Hengstenberg and

Mark calculated in 1930 for the first time mean micellar dimensions. At that time there was tendency to equate these dimensions, which were found for cotton with approximately 600 Å length and 50 Å thickness, with the length of the fiber forming molecules. Such interpretations caused Meyer to modify the Naegeli's model of micellar structure in the way shown by Figure No. 2.

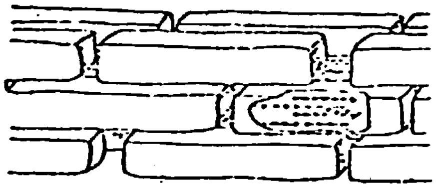


Fig. No. 2: Micellar structure according to Meyer.

The findings of Hermann Staudinger on the linear macromolecular nature of fiber forming molecules lead, however, very soon to another modification of this idea. From it developed the so called "fringed micellar theory" according to which the fiber is to be seen as a two phase system in which cristalline regions are tied to another by amorphous zones. Hereby the chain molecules of the fiber forming substance go through several cristalline regions alternatingly, as it is demonstrated in Figure No. 3.

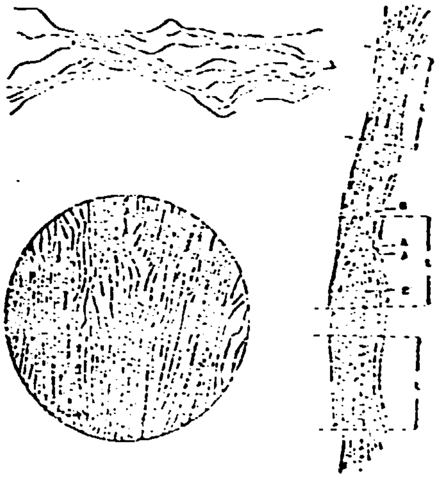


Fig. No. 3: Examples for fringed micell modells according to Meyer, van der Wyk and Mark.

In the beginning of the 1940's the development of the electrone microscope introduced a new phase in fiber structure research. With the electrone microscope one could recognize the existence of defined morphological units, namely of crystallites, of elementary fibrills, and of defined aggregations of them forming units of higher order.

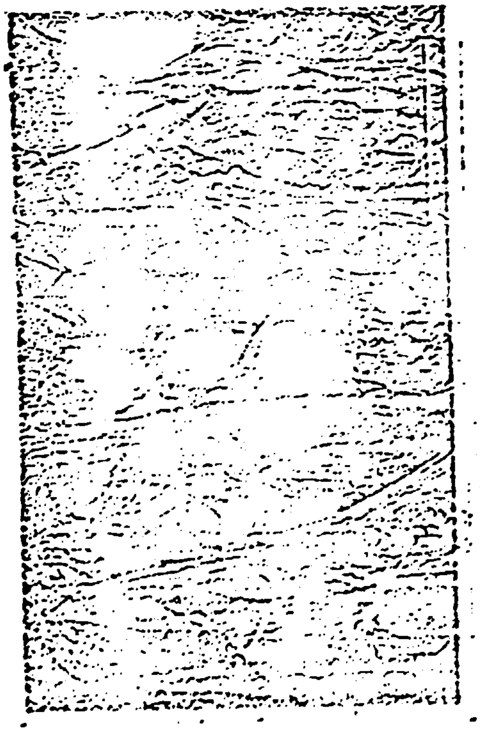


Fig. No. 4: Electrone micrograph of the fibrillar structure of cellulose fibers according to Ranby.

It is beyond the scope of this paper to enter into details on these results. The two electrone micrographs shown of partially degraded cellulose fibers and polyamide fibers respectively as Figures No. 4 and No. 5 demonstrate that the morphological structure of natural and of synthetic fiber is principally equal.

Fig. No. 5: Electrone micrograph of the fibrillar structure of polyamide fibers.

According to the results of newer research work linear macromolecules aggregate during fiber formation along a certain length and thickness, which depends on the chemical nature and the conditions during the fiber formation, to form more or less well ordered areas, the so called "cristallites". Because of the length of the molecules the cristallization will start at more than one position along the molecules at the same time, so that bands of cristallites are formed, which are tied together by less ordered transition zones. These bands of cristallites represent the so called "elementary fibrills". Several of such elementary fibrills will aggregate to morphological units of higher order.

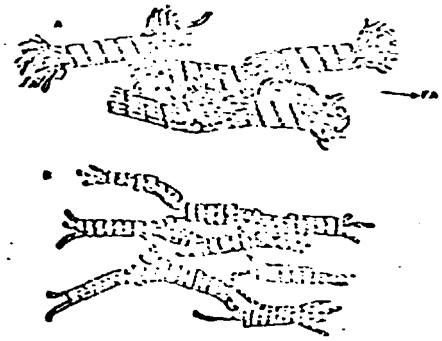


Fig. No. 6: Modells of fiber structure

A = fringed micellar structure

B = fringed fibrillar structure

These ideas of the morphological structure of man-made fibers which are widely accepted today are shown schematically in Figure No. 6.

Depending on the degree of order the assembly of these morphological units to the net-work of the fiber should come about either predominately by macromolecular segments of low order or by diverging elementary fibrills.

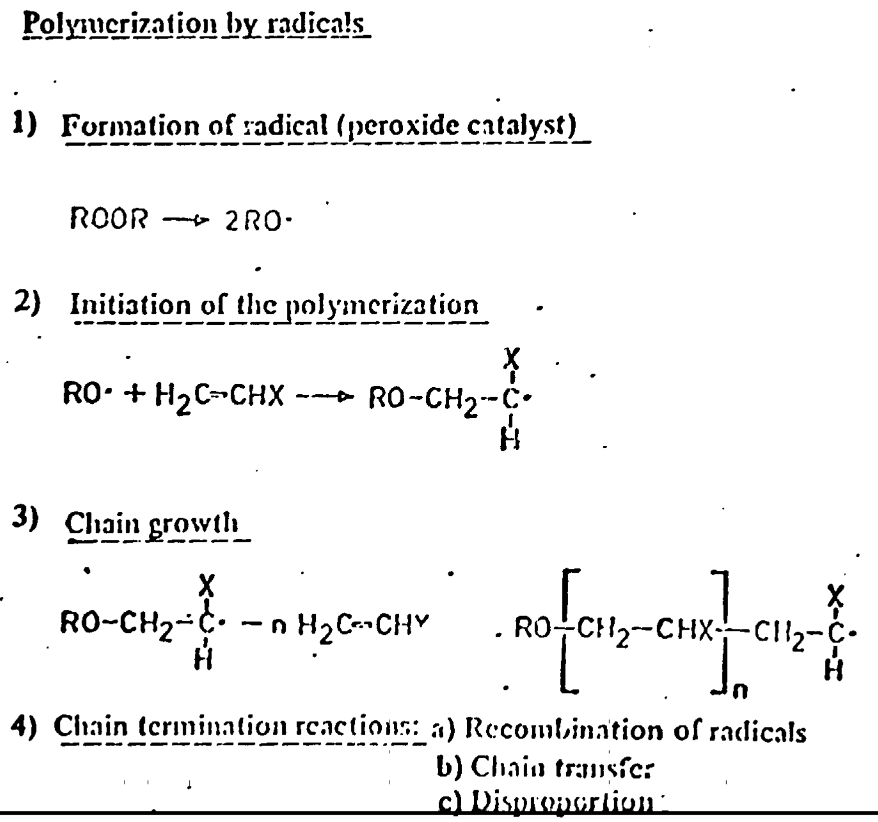
c) The synthetic fibers based on polymers made by polymerization:

The knowledge of the macromolecular nature of fiber forming substances and of the principles of the morphological structure of fibers have advanced the endeavours for a development of man-made fibers from synthetically obtained linear polymers.

They made possible the well aimed research for suitable synthetic polyme s and for endeavours to direct the fiber production with respect to optimum fiber properties. The knowledge of the fiber structure made it possible to influence the fiber properties through the degree of order in the structure units and through their orientation with respect to the fiber axis.

Three types of polymers aided by the ideas of Hermann Staudinger have gained importance for the development of fully synthetic fibers: polymers made by polymerization, by polycondensation, and by polyaddition.

Polymerization polymers are obtained by radical or ionic polymerization of unsaturated compounds, such as vinyl compounds. The reaction scheme of radical polymerizations is shown by the following formulas:



Polymerization by radicals

1) Formation of radical (peroxide catalyst)

$$ROOR \longrightarrow 2RO\cdot$$

2) Initiation of the polymerization

$$RO\cdot + H_2C{=}CHX \longrightarrow RO{-}CH_2{-}\overset{X}{\underset{H}{C}}\cdot$$

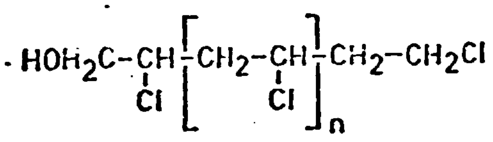
3) Chain growth

$$RO{-}CH_2{-}\overset{X}{\underset{H}{C}}\cdot - n\,H_2C{=}CHX \qquad RO\left[CH_2{-}CHX\right]_n{-}CH_2{-}\overset{X}{\underset{H}{C}}\cdot$$

4) Chain termination reactions: a) Recombination of radicals
b) Chain transfer
c) Disproportion

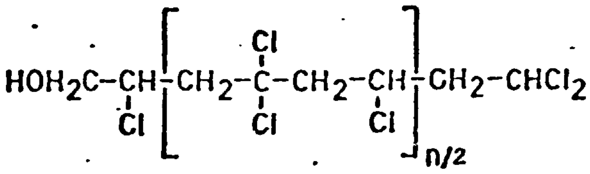
-19-

The first polymerization polymer finding attention for the processing of an artificially made fiber was the polyvinyl chloride. The chemical constitution of the polyvinyl chloride and the copolymer with vinylidene chloride is demonstrated by the following formulas:



$$HOH_2C-\underset{Cl}{\underset{|}{CH}}-\left[CH_2-\underset{Cl}{\underset{|}{CH}}\right]_n-CH_2-CH_2Cl$$

Polyvinylchloride



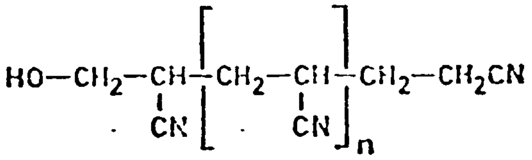
$$HOH_2C-\underset{Cl}{\underset{|}{CH}}-\left[CH_2-\overset{Cl}{\overset{|}{\underset{Cl}{\underset{|}{C}}}}-CH_2-\underset{Cl}{\underset{|}{CH}}\right]_{n/2}-CH_2-CHCl_2$$

Copolymers of vinyl chloride and vinylidene chloride

In 1931 Hubert and coworkers developed in the I. G. Farben plant Wolfen on the basis of a suggestion made originally by Klatte a wet spinning process for polyvinyl chloride solutions in cyclohexane. Because of the difficulties in the availability of cyclohexane at that time this process remained without success. Therefore, the process found by Schönborg in 1932 was a substantial advance. He suggested to use chlorinated polyvinyl chloride which is soluble in acetone. The mixability of acetone with water made it also possible to use water as coagulation bath and thus to simplify the large scale realization of the process. Later it was recognized that the increase in solubility of polyvinylchloride achieved by chlorination can also be obtained by copolymerization of vinyl chloride with vinylidene chloride which is the 1,1'-dichloroethylene. On this basis in the United States the so called "Saran" fiber was developed. Because of the increased solubility and the thus resulting better spinability also copolymers of vinyl chloride with vinyl acetate or with acrylonitrile ("Vinyon"- and "Dynel"-fibers, respectively) have come to importance. Later also the Société Rhodiaceta in France entered the development. Today polyvinyl chloride fibers are manufactured there under the name "Rhovyl".

Inspite of this, the polyvinyl chloride fibers have not been able to surpass a certain degree of importance. The total world production today is approximately 60.000 tons per year. All these fibers have in addition to good tenacity and elongation at break values also a high resistance against chemicals, infusorians and bacteria. They also show good flame resistance. A disadvantage is the relatively low softening point of approximately 170° C of polyvinyl chloride which limits the use of fibers made therefrom.

In the last two decades fibers made from polyacrylonitrile have obtained increasing importance. The following formula shows the chemical constitution of the polyacrylonitrile molecule obtained by polymerization of the acrylonitrile monomer (cf. page 21).



$$\mathrm{HO{-}CH_2{-}\underset{CN}{CH}{-}\left[CH_2{-}\underset{CN}{CH}\right]_n{-}CH_2{-}CH_2CN}$$

Polyacrylonitrile

The monomeric acrylonitrile has been synthesized in 1932 for the first time by Moureau. For its large scale production there exist today a series of processes. The oldest process is based on the synthesis of ethylene cyanohydrine from ethyleneoxide and hydrogen cyanide followed by splitting off water in the presence of magnesium carbonate or other water withdrawing substances. Another process makes use of the addition of hydrogen cyanide to acetylene. In a third process hydrogen cyanide is reacted with acetaldehyde. The most modern processes, however, make use of the reaction between propylene and ammonia in the presence of oxygen. It should be mentioned here that the economy of the production of synthetic fibers on a large scale depends on the industrial efficiency of the process for the production of the monomers used to synthezise the fiber forming polymer.

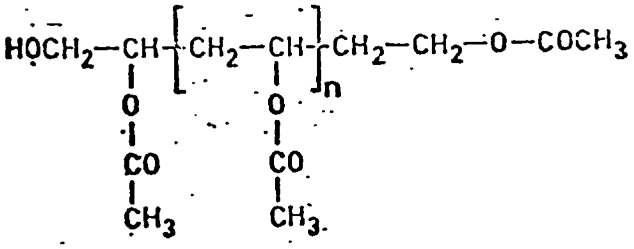
The polymerization of the monomeric acrylonitrile to polyacrylonitrile was worked out already at the end of the 1920'ies by the Badische Anilin and Soda Fabrik. Modern polymerization processes are based on the polymerization with the aid of persulfate catalysts in an aqueous emulsion or solution of the monomer. The polyacrylonitrile formed during the polymerization precipitates out and has to be separated off, dried and dissolved in suitable solvents. Recently interest has increased also for polymerization processes using solvents for the polymer in order to obtain a spinnable solution in a one step reaction.

Its non-meltability, temperature resistance and resistance against chemical influences have suggested early the thought of spinning polyacrylonitrile into synthetic fibers. The basic work for this was started in 1934 and was developed to a semitechnical scale during the years 1940 to 1943 by the I. G. Farben Industry. Already during the years 1935 to 1940 Rein found that polyacrylonitrile is soluble in concentrated salt solutions of the Hofmeister series, for example mixtures of zinc chloride and hydrochloric acid, as well as in quarternary bases of ammonia and that it can be formed to filaments and films from these solutions. In the year 1942 with dimethyl formamide a solvent was found that could be better used in a technical spinning process. Somewhat later the Du Pont Company in America began with work also using dimethyl formamide as solvent developing a special dry spinning process adjusted to the high boiling point of this solvent. With this process this firm is manufacturing on a large technical scale the so called "Orlon" fiber since approximately 1950. In Europe it was above all the Farbenfabrik Bayer which started to produce acrylonitrile fibers. Under the name "Dralon" they market a polyacrylonitrile fiber of very high quality.

The special properties of the polyacrylonitrile fibers are their high temperature resistance, their good resistance against chemicals and bacterial influences and their good light stability. In this respect they surpass even the polyamide fibers with which they can well compete with regard to tenacity, elongation at break and low water absorption. Initially, the difficult dyeability of polyacrylonitrile caused considerably difficulties. By copolymerization with small percentages of comonomers containing atom groups to loosen the structure and with groups that have affinity for dyestuffs these difficulties could soon be overcome.

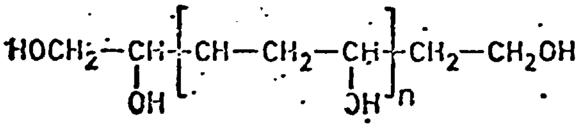
Today the polyacrylonitrile fibers have become next to the polyester fibers the synthetic fiber class with the highest growth rate. The world production of polyacrylonitrile fibers has in 1977 come close to 1,800.000 tons With regard to their appearance the polyacrylonitrile filaments are the most silk-like and the polyacrylonitrile staple fibers the most wool-like of all synthetic fiber materials. Today, however, staple fibers or converter tow are manufactured almost exclusively.

Among the fiber forming polymers obtained by polymerization as the next the polyvinylalcohol must be mentioned. The raw material for this fully synthetic polymer is vinyl acetate which is made from acetylene and acetic acid or rather the polymer obtained from vinyl acetate by polymerization. This polymer can be changed into the water soluble polyvinyl alcohol by acidic or alkaline saponification. The chemical constitution of polyvinyl acetate and of polyvinyl alcohol made from it by saponification is given by the following formulas:



$$HOCH_2-\underset{\substack{|\\O\\|\\CO\\|\\CH_3}}{CH}-\left[CH_2-\underset{\substack{|\\O\\|\\CO\\|\\CH_3}}{CH}-\right]_n CH_2-CH_2-O-COCH_3$$

Polyvinyl acetate



$$HOCH_2-\underset{\substack{|\\OH}}{CH}-\left[CH-CH_2-\underset{\substack{|\\OH}}{CH}-\right]_n CH_2-CH_2OH$$

Polyvinyl alcohol

The discoverers of polyvinyl alcohol, Hermann and Haehnel, were the first who tried in 1931 to spin filaments from its solutions. In fact it is possible to spin filaments with good properties in a wet as well as in a dry spin process. Since these filaments are water soluble and can therefore be applied only for quite special purposes, for instance as supplementary filaments to obtain certain textile effects, like alginate filaments, the main problem consisted in making the filament water insoluble in the course of the spinning process or by some after treatment. Among the hardening processes developed for this purpose the treatment with formaldehyde resulting in a cross-linking by methylene bridges is of special importance.

An application of the polyvinyl alcohol fibers for the normal textile end uses we find only in the United States and above all in Japan to a larger extent. Since several years Japanese firms have marketed under the name "Vinylon" polyvinyl alcohol fibers whose production has been very much promoted there. Today's total world production of polyvinyl alcohol fibers should be around 25.000 tons per year. It is hardly probable that this fiber will ever be produced at a rate as we know it from, for example, the polyester, polyamide or polyacrylonitrile fibers.

During the last years an additional class of polymers made by polymerization has gained practical importance for the manufacture of synthetic fibers, namely the polyolefins: polyethylene and to an even larger extent polypropylene.

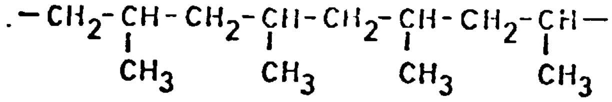
Until the middle of the 1950'ies polypropylene was only known as a paraffin-like soft substance melting at 75° C, therefore being of no technical importance. Only after Natta and Ziegler succeeded in finding catalysts such as aluminium and beryllium alkyl compounds being able to initiate stereo specific polymerization sterically uniform polypropylenes of high cristallization tendencies are being formed.
The structure of these sterically uniform polypropylenes is being demonstrated in the following formulas:
(cf. page 26)

-26-

Structure and properties of different polypropylene modifications

Softening temperature

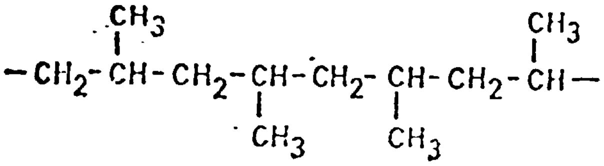
isotactic:



$$-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_2-\underset{CH_3}{\underset{|}{CH}}-$$

ca. 165 – 175°C.

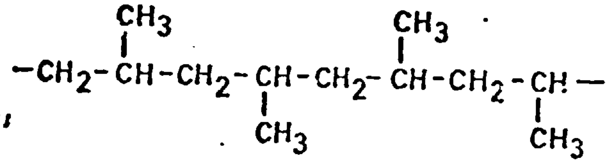
atactic:



$$-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_2-\overset{CH_3}{\overset{|}{CH}}-$$

ca. 70 – 75°C.

syndiotactic:



$$-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2-\underset{CH_3}{\underset{|}{CH}}-$$

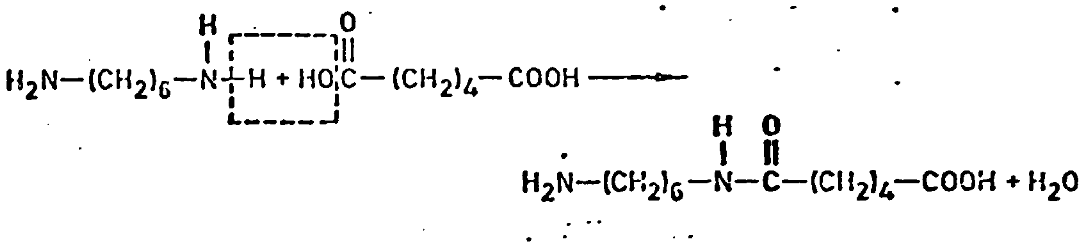
ca. 150 – 170°C.

The socalled "isotactic" or "syndiotactic" polypropylenes have high melting points in the order of 150 to 175° C, compared with the "atactic", sterically non uniform polypropylenes which only have a softening point in the range of 70 to 75° C. These high melting points allowed the use of these polymers for fiber production. The spinning of polypropylene fibers is performed today mainly by usual melt spinning. In certain cases fiber manufacture with the socalled split fiber processes via the film has gained importance. It should be mentioned that it is still difficult to dye polypropylene fibers by conventional bath dyeing and the low light and thermal stability affords the use of good and expensive stabilizers. The world production of spinneret spin polypropylene fibers today is in the order of 300.000 tons per year (1977). An additional approx. 200.000 tons of polyolefine fibers are made by splitting or slitting film techniques.

Of still greater importance for the development of synthetic fiber materials than the polymers made by polymerization were above all the polymer products made by polycondensation. The principle of polycondensation consists in the reaction of bifunctional compounds that can react with one another through the formation of water or some other low molecular compounds. The most important representatives of the fiber forming polycondensation products are the polyamides or the polyesters.

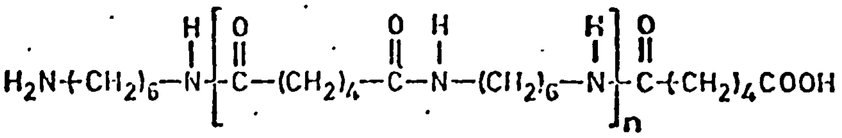
The principle of formation of polyamides is shown in the following scheme. The formation is based on the reaction of diamines with dicarboxylic acids with the formation of water. Thereby, amide groups are formed as connecting bridges which have given their name to this group of polymers.

The polycondensation of diamines and dicarboxylic acids to polyamides



$$H_2N-(CH_2)_6-\overset{H}{\overset{|}{N}}\boxed{-H + HO}\overset{O}{\overset{\|}{C}}-(CH_2)_4-COOH \longrightarrow H_2N-(CH_2)_6-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-(CH_2)_4-COOH + H_2O$$

by addition of more diamine and dicarboxylic acid molecules

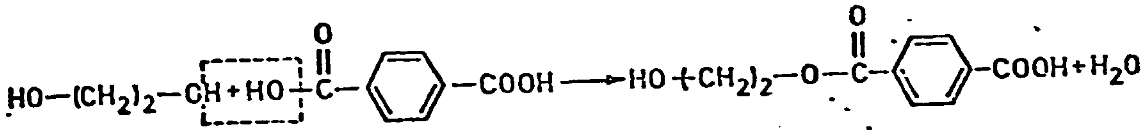


$$H_2N-(CH_2)_6-\overset{H}{\overset{|}{N}}\left[-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-(CH_2)_6-\overset{H}{\overset{|}{N}}-\right]_n\overset{O}{\overset{\|}{C}}-(CH_2)_4COOH$$

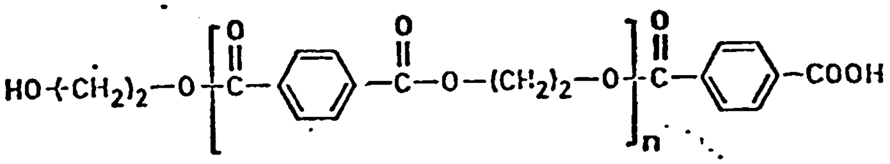
6,6 polyamide (Nylon)
is formed under elimination of water

In a similar manner polyesters are formed by the reaction of dialcohols with dicarboxylic acids under formation of water. The hereby formed connecting bridges are ester groups.

The polycondensation of difunctional alcohols and carboxylic acid to polyesters



by addition of more alcohol and carboxylic acid

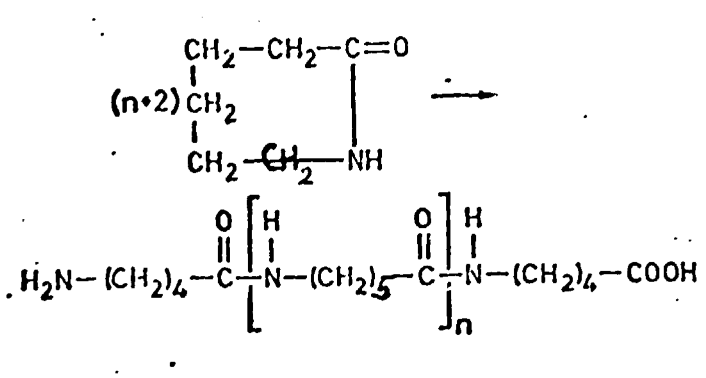


polyethylene terephthalate is formed under elimination of water (Terylene, Dacron, Trevira)

The development of the polyamide and polyester fibers is the most important result of the basic work of the American scientist Carothers. In the year 1929 Carothers working in the scientific laboratory of Du Pont started to investigate systematically condensation reaction which lead to the formation of ring systems and of linear high polymer compounds, initially without aiming at any technical application. Only in the year 1932 some observations of these investigations pointed in practical directions. Carothers observed at that time together with Hill that linear polyester of the ω-hydroxyundecanoic acid could be polymerized in high vacuum to form a particularly viscose and elastic high polymer from which flexible endless filaments could be drawn from the melt. Surprisingly, these filaments could be drawn in the cold state to a multiple of their original length and yet showed all typical properties of a true fiber. For example, in X-ray analysis they showed an excellently expressed X-ray diffraction picture. In addition to that, they had extremely good mechanical properties. Because of the low melting point, however, these filaments were not suitable for any textile end use. Carothers continued his investigation therefore at that time along a different line. He investigated at first the polycondensation of aminocarbonic acids and found that from poly-ε-aminocapronic acid a polyamide filament could be made which was quite similar to natural silk. This filament showed, however, still significant irregularities and under the impression of these difficulties in 1934 Du Pont was close to stop all together the investigations directed at a practical application. Only later it became known that the difficulties at that time were only caused by the insufficient purity of the aminocapronic acid. Similar polycondensation experiments with 9-amino nonanoic acid brought about in this decisive moment the success needed for the continuation of the work. In 1935 Carothers succeeded finally to find in the polyamide formed from adipic acid and hexamethylene diamine the polycondensate which conquered as "Nylon" in the following years the whole world. This polyamide became, due to its good fiber properties, its sufficiently high melting point and its favourable raw material basis - phenol and benzene respectively - a guiding post for the following technical development in the synthetic fiber field. However, three more years of development were necessary to come up with a melt-spinning technology suited to the high melting temperature, whereby the known methods to produce glass fibers were of valuable assistance.

In Germany at the I. G. Farben Industry and its associated plants the development followed a somewhat different course. Although, already in the year 1928 first trials had been made to produce polycondensation products and to process them into fibers. However, the work had also been abandoned before long because of rising difficulties. After the publication of Carothers' patents in the year 1937 one turned decidedly back to it with the aim of producing a new synthetic fiber by the way of polycondensation polymers. Early 1938 the work of Paul Schlack then lead to the discovery of a "polymerization process" for ε-caprolactam, which follows the outline shown below:

The 'polymerization' of caprolactam to 6-polyamide:



6-polyamide (Perlon)

Following that, a severe patent dispute arose with the American firm Du Pont de Nemours about the issue whether the ring opening reaction of caprolactam to form polymprolactam is to be regarded as a condensation reaction by intermediate formation of ε-aminocapronic acids by reaction with traces of water. In this case the process of the I. G. Farben Industry would have been already covered by the patent of Carothers. Schlack and his coworkers succeeded, however, in proofing that in this case the polymerization process occurs also when absolutely no water was present. A compromise was reached and the two opponents agreed on a long lasting exchange of know-how and licences in the field of polyamides. In fall 1939 polycaprolactam monofils were marketed as first products on this basis in Germany under the name of "Perluran" or "Perlon L", respectively. Polyamide fibers were for a long time the leading fully synthetic fiber material. The world production of polyamide fibers has reached in 1973 a total of approx. 2,95 (1977) million tons, whereby the greater part (about 80%) was in form of filaments and only a smaller part in form of staple fibers. The main end uses of polyamide fibers are in the area of ladies hosiery, light weight knit wear and blouses, as well as the application as industrial filaments for ropes, conveyor belts and tire cord.

While Carothers did not succeed to find a polyester useful for industrial production, the Englishmen Winfield and Dickson were successful in this respect in 1946. By polycondensation of terephthalic acid with ethylene glycol they arrived at a polyester whose melting point lay substantially above 200° C and which could be melt spun and drawn into fibers with good properties. Especially remarkable in this product was its high resistance against saponifying agents.

It was difficult to solve the problem of providing the raw materials for this product, especially to solve the problem of the large scale production of terephthalic acid, although they had been known for a long time. However, in the meantime a series of economic processes have been found to produce terephthalic acid by oxydation of para-xylene or of toluene, both of which can be obtained from petroleum products.

In the early 1950'ies the Imperial Chemical Industry Ltd. in England built the first polyester fiber plant and started to market a fiber under the name"Terylene".

In the meantime the polyester fiber on the basis of polyethylene terephthalate has become the most important competition of the polyamide or "Nylon" fibers and all big producers of synthetic fibers have also built production plants for this type of fiber, such as Du Pont with "Dacron" or Farbwerke Hoechst with "Trevira".

The world production of polyester fibers has surpassed in the year 1968 for the first time the one million ton limit and with the production of 2,6 million tons in 1973 the production of polyamid fibers. In 1977 a total of 4,2 million tons of polyester

The polyester fibers have penetrated a large sector of the clothing market. Above all it became aparent that especially mixtures between polyester and cellulose fibers result in textile materials with pleasant wear properties and good durability.

3. The economic importance of man-made fibers:

The great importance man-made fibers and among them especially the synthetic fibers have obtained in the above described third phase of development, which took place in the last three decades, can best be seen in regarding the development of the world production of the individual fiber types.

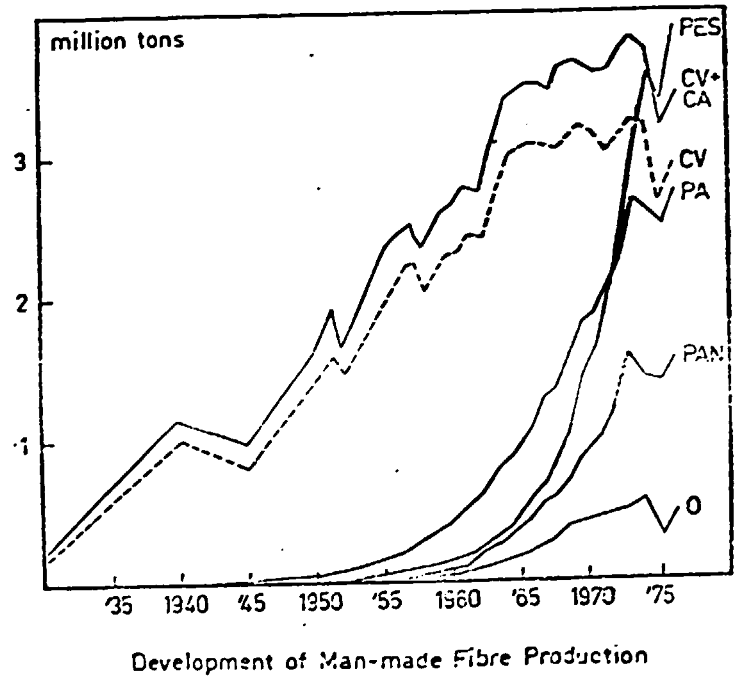


Fig. No. 7: The development of the world production of various man-made fiber types during the last 40 years.

A close study of the development shows that in the years 1950 to 1960 the man-made fibers on the basis of cellulose have taken an immense upswing which can well be compared with the spectacular development of the synthetic man-made fibers in the last decade. Man-made fibers on the basis of cellulose are today still the largest single man-made fiber class and it will take yet some years until the production of polyester, polyamide or of polyacrylonitrile fibers each of them taken by itself will have reached the same level as the production of man-made fibers on the basis of cellulose.

The stormy development of man-made fibers during the last years will certainly continue and the time when man-made fibers will have reached the volume of natural fibers can be expected already for the next few years. The rising standard of living in wide areas of the world and the continuously growing world population demand such development because the natural fibers would not be in a position to satisfy the rapidly growing demand for textile and technically used fibers. There exists a series of forecasts for such a development. In the table shown below the results of thoseforecasts, which have become known to us, are listed:

Future development of natural and man-made fibers

Year	Cotton		Wool		Man-made fibers				Total
					Synthetics		Cellulose fibers		
	1000 to	%	1000 to	%	1000 to	%	1000 to	%	1000 to
1970	11.100	52	1.505	8	4.870	23	3.700	17	21.265
1980	12.200	40	1.600	6	12.000	39	4.600	15	30.600
1990	13.300	32	2.000	5	20.000	50	5.500	13	41.600

From this table one can see that the synthetic man-made fibers have developed within the last 20 years to an important factor of the fiber market and cover already more than 30 % of the total fiber production today. Together with the man-made fibers on the basis of cellulose, man-made fibers represent all-together already more than 40 %. For the year 1980 the total production of man-made fibers is estimated to be approximately 15 to 16 million tons which corresponds to more than 50 % of the total world fiber production. According to careful estimates still more than one third of this will be man-made fibers on the basis of cellulose. The demand for cellulosic fibers should increase with a rising production of synthetic fibers and in return influence their development because the importance of fiber blends for the production of textiles with optimum wear comfort.

For the year 2000 a total fiber production of more than 50 million tons is estimated of which approximately 75 % will be man-made fibers. More than 30 million tons of fully synthetic man-made fibers are placed for this time against approximately 6 to 8 million tons of man-made fibers on the basis of cellulose.

In talking about the significance of man-made fibers it must be mentioned that man-made fibers as a whole have brought to the textile industry and to the manufacturers of industrial fiber products a significant enlargement of the fiber assortment and that thereby it has been possible by selecting the most suitable fibers to reach an optimum of end use properties.

On the other hand it must also be stated that until today it has not been possible to create an universal fiber which combines in itself all desirable properties at an optimal level. It is in our opinion not to be expected that in the near future such an universal fiber can be created. At a round table discussion at the International Man-made Fiber Conference in Dresden in the German Democratic Republic with the topic "Man-made fibers in the year 2000", the assembled specialists agreed on the fact that the creation of such an universally useful fiber type is improbable for a variety of reasons and seems also hardly desirable. The efforts to eliminate one of the most essential disadvantages of the thus far known fully synthetic man-made fibers, namely the insufficient capability to absorb and desorb water could lead to the realization that reaching this goal is only possible by sacrificing some other advantageous properties, as for example, the high wrinkle resistance, the high wet tenacity, the good dimensional stability and others. A single ideal fiber would perhaps not be desirable because by its existance the variety in fashion which the textile industry can create today with the variety of various fiber types could get lost, a fact we all would regret.