

YFARS

OCCASION

This publication has been made available to the public on the occasion of the $50th$ anniversary of the United Nations Industrial Development Organisation.

TOGETHER

for a sustainable future

DISCLAIMER

This document has been produced without formal United Nations editing. The designations employed and the presentation of the material in this document do not imply the expression of any opinion whatsoever on the part of the Secretariat of the United Nations Industrial Development Organization (UNIDO) concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries, or its economic system or degree of development. Designations such as "developed", "industrialized" and "developing" are intended for statistical convenience and do not necessarily express a judgment about the stage reached by a particular country or area in the development process. Mention of firm names or commercial products does not constitute an endorsement by UNIDO.

FAIR USE POLICY

Any part of this publication may be quoted and referenced for educational and research purposes without additional permission from UNIDO. However, those who make use of quoting and referencing this publication are requested to follow the Fair Use Policy of giving due credit to UNIDO.

CONTACT

Please contact publications@unido.org for further information concerning UNIDO publications.

For more information about UNIDO, please visit us at www.unido.org

Marken Str. Dr. assistants **SECTIONARY** \hat{a}

ï

 $\bar{1}$

79726

The Economic and Technical Future of Man-Made Fibers by Dozent Dr. Hans Krässig, Director of Research and Development of Chemiefaser Lenzing AG

During the last two weeks you have been informed in a number of lectures and laboratory sessions on the chemistry, physics, technology, testing and application of man-made fibers. From this you have learned that todays textile industry could not fulfill its task without man-made cellulosic fibers or without the wide variety of synthetically produced artificial fibers.

The Economic Future of Man-Made Fibers I_{\bullet}

In the first paper of this seminar, which was read to you in my behalf by my colleague, Dr. Teichmann, the following figure No. 1 was shown to you illustrating the past development of manmade fibers.

Development of the world, production of man-inade fibers since 1936.

ລ

You may recall that the start of the development of man-made fibers goes back to the end of the 19th century, where the first artificial cellulosics were being developed. However, the actual technological breakthrough only occured in the mid thirties after Hermann Staudinger's ideas of the chain-like macromolecular structure of natural and synthetic fiber-forming compounds, such as cellulose, proteins, polystyrene, polyvinylchloride and others were acknowledged and accepted. From there *on,* first the man-made fibers based on cellulose, such as the viscose and cuprammonium fibers as well as the cellulose acetate fibers, started their rapid development, which during the late forties and throughout the fifties was not less spectacular then the rise of the purely synthetic fibers in the last two decades. You should be aware of the fact that still today the man-made fibers based on cellulose are still the largest single grcup of artificially produced fibers - still ahead of polyesters, polyamides, polyacrylics and all the other synthetics.

I I

Ĺ,

 \bm{l} ,

The development of the synthet c fibers - the polyamide $6,6$ and 6, the polyethyleneterephthalate polyester, the polyacrylics and the others - actually started only after the second world war and at the beginning also relatively slowly. The rapid increase in wo~ld production of synthetic fibers started around the year 1960. From the development during the last years it can be clearly seen, that the development of polyamide fibers begins to flatten out, while the polyester and polyacrylic fibers still increase at a remarkable pace. This reflects the fact that polyester and polyacrylic fibers are gaining increasing acceptance in the clothing, the drapery and the carpet market.

 \overline{z}

- 2 -

At the end of your seminar it seems appropriate to me to make you look into the future of man-made fibers and to outline to you at least in general terms the presently apparent development trends in the man-made fiber industry.

One thing is without doubt: The rapid development of man-made and especially of synthetic fibers will and will have to continue. Without man-made fibers it would in the future never be possible to adequately cloth and supply the rapidly growing mankind. The world population in 1850 amounted only to 1,5 billions. To double to $3,0$ billions it took one hundred years until 1950. It will now only last 30 years until 1980 when the world population will double again reaching 6,0 billions. What effect the measures to control this "population explosion" discussed throughout the world, will actually have can not be estimated. In any case, however, at the end of this century approximately 7 to 8 billions human beings will populate this globe.

,, !!
'

》

The yearly world production of natural fibers, such as cotton, wool, or silk, however, has grown during the last seventy years only linearly. This is shown in the following figure Nc. 2.

-4 ..

I

- 3 -

 $\widehat{\mathbb{C}}$

 $\overline{\mathbf{C}}$

Development of yearly world production of natural fibers

From the data of the yearly production of natural fibers the theoretically possible textile supply per head of the world population can be calculated. As can be seen from the following figure No. 3 the supply of natural fibers until 1930 has been sufficient to satisfy the textile needs.

Development of worldwide yearly per capita consumption of fibers and the supply situation by natural fibers

However, from thereon an increasingly widening gap between the available supply of natural fibers and the fiber demand exists. This gap between the textile needs of the rapidly growing world population and the natural fiber supply will become larger and in the year 2000 natural fibers can only satisfy approximately one quarter of the fiber needs of mankind. Without the man-made fibers it would increasingly be impossible to cover the demand increased by the rapidly growing world population and the increasing living standard throughout the world.

 $-6-$

It seems worthwhile to take a short look at to the reasons preventing an increased growth of natural fiber supplies. The major reasons named are the following:

1. The probability that agriculturally used land will have to be used in the future to an increasing extent to satisfy the needs of mankind for food. Surely, this should not be overemphasized, since the pussibility exists to develope large additional areas throughout the world to agricultural use by proper irrigation, replanting and reforestry measures

 \mathbf{f}

..

- 2. The increasing movement of people away from the relatively hard work in the fields to job in the industry and in general service professions calling for a structural change and for heavy investments to introduce automation and mechanisation in the agricultural area.
- $3.$ The increasing apparent problem of maintaining the yields on agriculturally utilized land.
- Most experts agree that such reasons may even bring upon a slow, but steady decrease in natural fiber supply towards the end of this century.

Since the later part of 1973 with the socalled " $v1$ crisis" and the accompanying drastic incleases in the prices for petroleum, petrochemicals and energy production, the man-made

-7-

fiber growth especially that of synthetic fibers is in itself endangered. This changed situation let man-made fibers, based on natural raw materials constituting themselves in short time periods, such as wood cellulose, appear in a new light. But here one should also consider the fact that only approximately 5 % of all the petroleum used are utilized for chemical purposes. Therefore it seems unlikely that a shortage in chemical supplies will hinder in the near future the development of synthetic fibers.

From the development of world population and from a linearly increasing consumption of fibers per head one can easily and without too much speculation estimate the world production of natural and man-made fibers needed until the year 2000 to satisfy the needs. The figures derived in this way are shown in the following figure No. 4.

to a metric tons

Preview of the development of the world fiber production between $1970 - 2000$

-8-

This figure illustrates that the world production of fibers will have to increase from approximately 20 million metric tons in 1970 to over 30 million metric tons in 1980, to approximately 42 million tons in 1990, reaching somewhere over 50 million metric tons in the year 2000. The share of man-made fibers in these totals will increase from about 40 % in 1970 to nearly 70 % in the year 2000.

•

-9-

i

II. The Technological Future of Man-Made Fibers

 \mathbf{C}^{λ}

 $\big($

These considerations outline to you the economic importance of man-made fibers for the mankind and for the future techn logical development. It therefore seems appropriate to me to outline to you shortly the future technological development trend already apparent in the man-made fiber industry. In doing this, I have to point out to you that in the time left to us I can only give you a very sketchy image of the future trends which in no respect can claim completeness.

The presently apparent development trends in the man-made fiber industry can be summarized as follows:

1. Development Trends for Conventional Man-Made Fibers

- Establishing rational production capacities (over 10'000 metric tons for continuous filaments; over 30'000 to 50'000 metric tons for staple fiber production).

- Rationalization and process improvement (especially with respect to low raw material and energy consumption, to the solution of environmental problems and with respect to advanced technology, such as "spin-stretch technology" or "spin-texturing technology", etc.)

- 9 -

- Development of specialized fiber types (for application areas large enough to justify such "Fiber Engineering" efforts and calling for fiber properties better suited to end use requirements)
- Well directed efforts for improvement of existing fiber types reducing known shortcomings, such as:/

For cellulosics:

•

Better dimensional stability, better crease resistance, better crease recovery, fuller hand, reduction of water retention, differential dyeing properties (deep dyeing types;acid dye affinity), reduced flammability, etc.

For synthetic fibers:

Increased water absorption, improved hand (more textile touch), **International Property**

better antiztatic properties, reduced yellowing terdency, reduced soiling, improved cleaning properties, reduced pilling tendency improved dyeability, development of fibers with altered dye affinity (differential dyeing characteristics), reduced flammability, non-melting types, etc.

2. Development Trends for New Types of Man-Made Fibers

- Development of fibers from newly found fiberforming polymers,
- Development of specialized fibers from new polymers with properties specifically designed for given end uses (so far application areas are large enough to justify such "Fiber Engineering", e. g. \bullet
	- ... Fibers with rubber elassicity,
	- ... Fibers with latent crimp properties, e.g. bicomporent fibers,
	- ... Improved tire cord fibers (non-flat-spotting),
	- ... Fibers with extreme high modulus (fiber reinforced composites),

-11-

I

 $\mathbf C$

•.

C'

- ... Fibers with high temperature resistance,
- ... Non-melting and flame resistant fibers,
- ... Fibers with electric conductivity or with semiconducting properties, etc.
- Development of advanced polymer synthesis methods (such as matrix polymerisation, simultane ous polymerization and fiber formation, etc.) and of new fiber forming and processing technologies (film slitting or splitting techniques; spun-tonded products).

In the following I would like to illustrate to you these development tendencies on a few selected samples.

•

It is the widely accepted opinion of most fiber experts that solving the problems of reducing raw material and energy needs in fiber production and adjusting to the more stringent environmental protection measures will determine and consume a large portion of the research and development efforts during the coming years. I would easily take another two weeks, would we attempt , to discuss in more details the problems the man-made cellulose fiber industry and the synthetic fiber industry has to cope with in their efforts to solve these problems.

We will therefore restrict our discussion to the efforts of the man-made fiber industry for fiber improvements and for new fiber developments. All experts agree that these efforts will in

-12-

. general be directed towards and characterized by the socalled "Fiber Engineering". The term "Fiber Engineering" designates the search for fibers with properties specifically engineered for certain end uses. This "Fiber Engineering" has - so far the modification of already existing fibers is concerned - already determined the last two decades of man-made fiber developments often named as the "area of second generation man-made fibers".

a) Development Trends in the Cellulose Fiber Industry

..

(

"

 $\left(\Gamma\right)$

One fact should not be overlooked: Pace-maker of the "Fiber Engineering" has been the good old viscose fiber industry. In this connection we should recall the efforts for high tenacity cellulosic fibers, which already started in the first decade of this century with the development. of the socalled "Lilienfeld Process''. These high-tenaoity cellulose fibers did at that time not find acceptance due to their high defibrillation tendency. In the first years of the f ifthies chemists of the American company Du Pont de Nemours found additives - socalled "modifiers" to the viscose spinning solutions retarding regeneration and cougulation during fiber formation and allowing the application of • high stretch ratios. This modification resulted in high-strength cellulose fibers having elongations of over 10 %. This important discovery has broken with the old prejudice that cellulosic fibers of high strength always show low elongation and high defibrillation tendency. As result of this discovery che properties of viscose tire cords could be remarkably improved, as can be seen from figure No. 5 (cf. page 13).

-13-

- 12 -

Development of viscose tire cord strength from 1953 to 1961

The oven-dry tenacity was improved in the years 1953 to 1961 from 27 lbs to nearly 40 lbs for 12/12 cord. These improvements gave the viscose tire cord a strong position in its competition with nylon tire cord and against all expectations viscose tire cord still holds its share in this very competitive field.

The discovery of the Du Pont chemists, however, stimulated also the development of high strength viscose fibers for textile use. These efforts resulted in the last ten years in the development of the socalled "High Wet Modulus" and the "Polynosic" fibers, which are already well established in the market. A good number of the goals for improvement of man-made cellulosic fibers, named to you a short time ago, have been largely achieved in these

 $-14-$

modern, improved viscose fiber types. They show, as illustrated in the following figure No. 6, largely reduced water retention properties, resulting in better dimensional stability, fuller hand, improved crease resistance and better wash wear characteristic in fabrics made therefrom.

Water Retention of Various Man-made Cellulosic Fibers Tx = Regular Rayon Po = Polynosic Tr = Viscose Tire Yarn $M =$ Meryl HM= High Wet Modulus **Bw: Cotton** F = Fortisan

These improved viscose fibers have gained special importance in their use as blending partners with cotton or with polyester, since their stress-strain behaviour in the conditioned and in the wet state matches well that of cotton and of polyester fibers, as you can see from the following figure No. 7 (cf. page 15).

 $-15-$

Stress-strain Properties of High Wet Modulus Rayon

The discovery of the "Viscose Modifiers" and the modern viscose spinning technology they initiated, have principally open the gates for systematic "Fiber Engineering" of man-made cellulosic fibers in better accordance with end-use requirements. In Figure No. 8, shown here, I have summarized for you the wide variety of viscose fiber types the cellulose fiber industry can supply today having tenacities between 2,0 g/den up to nearly 9,0 g/den, elengations between $7 \frac{2}{3}$ and $30 \frac{2}{3}$, etc. (cf. page 16).

 $-16-$

STRUCTURE AND PROPERTIES OF VARIOUS REGENERA ULOSE FIDERS

These variations in properties actually were achieved by appropriate adjustments of the spinning process to the use of celluloses of varying degrees of polymerization, to achieve a desired degree of order or "crystallinity" and a desired degree of orientation. Today it is possible for the case of cellulosic fibers to explain. mechanical and end-use performance on the basis of these structural characteristics.

. Also the efforts of the viscose fiber industry for better crimped fibers for the blanket and carpet industry can be termed "Fiber Engineering". The improved crimp and the improved crimp recovery especially on wetting and drying was achieved by establishing a quasi "bicomponent structure". This bicomponent structure can be produced by special coagulation and regeneration conditions in fiber spinning and by the application of a special stretching technique (cf. figure No. 8, page 17).

 $-17-$

Structure of the cross-sections of normal crimped viscose staple fibers (left; "skin-" core"-structure) and of advanced crimped viscose staple fiber types, such as Lenzing's TAPIFLOR (right; "bi-component"-structure).

 17

By these spinning conditions the fiber skin formed in spinning is caused to rupture allowing the plastic and differently structured core to protrude ot the fiber surface.

In the last years other goals for "Fiber Engineering" gained importance as well for the manufacturers of man-made cellulosics as for synthetic fibers, namely the development of fibers of altered dyeing characteristics - socalled "differential dyeing" properties - and the development of fibers with flame-retardant properties. The interest in fibers with differential dyeing characteristics was initiated by the efforts of carpet manufacturers and other textile processing people to rationalize finishing and styling procedures. The application of fiber types having different but specific affinities to various classes of

 $-18-$

dyestuffs allows the carpet or fabric manufacturer to produce styled carpets or fabrics from colorless but differentially dyeing yarns which can be dyed in one operation in multicolor shades by using dyebaths containing mixtures of the corresponding *:* dyestuffs. By using dye-baths of varying dye compositions one can produce from the same colorless carpet or fabric complete collections in a short time and in close coordination with the demands of the consumers. During the last years public discussions have caused the governments in many countries to take legislative measures banning flammable fabrics and other textile products. In the United States of America flammability standards are already in effect for carpets, for children's nightware and for fillings in mattresses.

For producing cellulosic fibers with differential dyeing characteristics, such as "deep dyeing" or affinity to acid dyestuffs two principle methods are being applied. One being the purely physical incorporation. of compounds increasing the accessibility for dyestuffs or to introduce anionic sites into the fiber. Such compounds are water or alkali soluble polymers,, e.g. polyamines, polyamides, polyvinylpyrrolidone, and others. The second method is the introduction of structure opening substitucnts or of dye receiptive atom groups containing substituents by chemical reaction, such as etherification, esterification or by grafting, e.g. with acrylamide, with vinylpyridine or with vinylpyrrolidone.

. '

..

-19-

It may be mentioned here, that grafting of polymer side chains to cellulose has become possible during the last years by applying the socalled "xanthate-peroxide"-grafting method invented by Faessinger and Conte of Scott Paper Company. This method is based on the radical transfer tendencies of xanthate groups enhancing grafting efficiency. The mechanism of this graft initiation is given by the following figure No. 9.

 $-20-$

IF

I

•

By a special way of heat transfer this type of grafting can be performed with polymer add-ons of approximately 30 % in a matter of seconds allowing grafting in line during fiber manufacturing.

In the case of textile goods with flame retardant characteristics there exists surely the possibility of flameproofing fabrics and knits in course of textile finishing operations. So far the end use requirements do not call for permanence and laundering stability this is without problems and can be achieved by impregnation or reaction with suitable finishing agents, such as ammonium phosphates, antimon oxide, tetrakis-(hydroxymethyl)-phosphonium chloride, N-methyloldialkyl-phosphono propionamide, and others. The chemical composition of some of these compounds is given in the following figure No. 10.

However, when the end use calls for good permanency and good stability in repeated laundering one has to stabilize the flame retardant chemical onto the fabric by applying them in combination with heat setting resins. This causes losses in wear resistance, in textile hand and in wear comfort as generally experienced with "wash-wear" or "permanent press" treatments of cottcn or other cellulose fabrics. In these cases the application of flame retardant fibers is highly recommended.

). The contract of the contract of

- 21 -

Flame retardant man-made cellulose fibers can be produced, similarly to differential dyeing fibers, by either simple physical incorporation of flame retarding compounds or by chemical substitution or grafting with substituents or polyn.er side chains carrying atom groups acting as flame retardant.

 \bullet

 \bullet

For the physical incorporation via addition to the viscose spinning solutions phosphorous, nitrogen or halogen containing compounds are suited. Some examples of such compounds exerting flame retarding actions are given below (cf. figure No. 11).

.I -0 - CH₂ - CHBr - CH₂Br
= P - 0 - CH₂ - CHBr - CH₂Br $\mathbb{P}_{\infty}^{\mathbb{P}_2}$. '' H₂-CHBr-CH₂Br Tris-2.3-di brompropyl-phosphate $Proo P$ χ^r s χ^r $N < \sqrt{N}$ $\begin{array}{ccc} Pr0 & | & | \text{OPT} \\ \text{PP} & P & \text{OPT} \end{array}$ Pro^{/ "}N^{/ "}oPr' Phosphornitrile-hexapropyl ester

Examples of Flame Retardant Viscose Additives.

i I

-22-

A requirement such compounds have to fulfill is water insolubility.

In the United States the Southern Regional Research Laboratory in New Orleans is doing quite interesting work to introduce flame retardant characteristics into cellulose fabrics by a direct phosphorylation methods.

Also by grafting with polymerizable monomers containing phosphorous, nitrogen or halogen atoms highly flame retardant cellulose fibers can be produced. The principle of the chemical composition of such modified fibers is given by the following figure No. 12.

 $-22 -$

Since you are visiting here a company which today is one of the largest viscose staple fiber manufacturer, it seems adequate to also tell you what new things and new developments are going on in this field. In many respects cellulose fiber developments have in the past and still do today initiated new scopes in the man-made fiber industry.

b) Development Trends in the Synthetic Fiber Industry

In the field of acrylic fibers the development efforts were mainly directed towards polymer modification for better thermal stability and specific dyestuff affinities in the sense of "differential dyeing" characteristics. The use of acid groups containing comonomers, such as p-styrene sulfonic acid, enhances dyeing with anionic dyestuffs, while the use of basic groups containing monomers, such as 2 -vinylpyridine, introduce dyeability with cationic dyes, as you can see from figure No. 13.

 \blacksquare

I •

 $CH = CH₂$

p-Styrene sulfonic acid 2 - Vinyl pyridine

I

Each company involved in acrylic fiber manufacturing devotes a good part of its development effort into exploring the use of new monomers and monomer combinations in order to achieve a good compromise between good fiber formation, improved thermostability and good dyeability. With respect to the development of flameretardant acrylic fibers copolymerization of acrylonitrile with substantial portions of halogen containing monomers, such as vinyl chloride or vinylidenchloride, have been successful. These socalled "modacrylics" have already conquered a good share of the market for flame retardant fibers (cf. figure No. 14).

ſ.

Structures of flame-retardant "Modacrylics".

- 24 -

The development efforts of the manufacturers of polyester fibers today follow also mainly the line of "Fiber Engineering". They are principly directed towards the development of polyester fibers with "differential dyeing" characteristics, towards the development of polyester fibers with reduced pilling tendency and towards polyester fibers with latent α imp properties.

The efforts for polyester fibers with specific dyeability aim in three directions:

- Increased receptivity for dispersed dyes through the development of copolyester types using small proportions of other base units than ethylene glykol and terephthalic acid. A selection of other base units used for producing copolyesters giving fibers with enhanced dye receptivity is given in the following figure No. 15.

- Affinity towards cationic dyestuffs by the development of copolyesters with increased numbers of acidic sites. A number of modified dicarbonic acid or of modified diols used for this purpose is listed in the following figure No. 16 (cf. page 26).

1) Einbitu der Cokomponente bei der Polymerherstellung ноос \sim соон ั∑ }∋‱ $X - CH_2 - CH_2$ CH₂-CH₂-X ė $R = -50$ ₃Na₂ -R-50₃Na₂ -50₂Na₂ -50₂O-C₆N₉ $x = 4x - 600$ $-90(60n)$. -0.0 -0.001 $HOCH_2 - P - CH_2OH$ ноос $\langle \rangle$ р \Diamond соон ONO 2) Inkorponeren von anionenaktiven Substanzen vor ader während des Soinnprozesses 3) Nachbehandlung von Faden und Fasern mit S01, S02Cl2 und Cl S02H Mit kationischen Farbstaffen färbbare PÄT-Fasern

- Affinity towards cationic dyestuffs by the development of copolyesters with increased numbers of anionic sites. Examples of modified dicarbonic acids and diols are listed below. The list also contains incorporation compounds and chemical reactions used to physically or chemically modify conventional polyesters (cf. figure No. 17).

Œ,

 $\bar{1}$ and

For the development of polyester fibers with reduced pilling tendency various routes have been taken:

- The use of conventional polyesters of short chain length. Fibers made from polyesters of lower molecular weight still show reasonable tenacity but sharply reduced bending strength.

 $\bar{1}$

 $\alpha = 1$

and the con-

 $\bar{1}$

 \sim

 $\alpha = 0.4$

 $-27-$

 \sim \sim

 $-26 -$

- The use of copolyesters with $10 15$ % isophthalic acid, phydroxy- or p-hydroxyethoxy benzoic acid or containing endstanding biocks of polyethylene oxide.
- The use of polyesters slightly crosslinked or branched by the use of polycarbonic acids or polyalcohols in the polycondensat ion.

The efforts for the development of high shrinkage or high bulk polyester fibers center around two principle ways, namely:

- Introduction of shrinkage properties by physical means into normal polyesters, such as overstretching treatment. When such fibers are treated above their original fixation temperature they will contract.

,

- The use of copolyester fibers containing low percentages of other dicarbonic acids or difunction alcohols, altering the cristallisation kinetic allowing highly stretched fibers to move easily contracted when treated above their original fixation temperature.

One fact become5quite apparent. These modifications for differential dyeing characteristic, for lower pilling tendency and for higher shrinkage all bring out the potential of using modified copolyesters for the ''engineering" of polyester fibers.

-28-

- 27 -

Aside these efforts the polyester fiber industry Jrives for permanent antistatic polyesters and for polyesters with reduced flammability.

In the polyamide fiber industry similar development trends have become apparent to modify conventional polyamides - nylon $6,6$ or nylon 6.

These efforts center mainly around the following three routes:

,

 $\mathbf{\mathcal{C}}$

- The structure modification of conventional polyamide fibers by physically incorporated additives. This principle is being used for introducing antistatic agents or agents changing dyeability characteristics.
- The use of copolyamides or of mixtures of differently structured polyamides. In such efforts differently structured dicarbonic acids or diamines are being used in combination with adipic ac and hexamethylene diamine or with caprolactame. By this route also differential dyeing effects, better antistatic properties, altered shrinkage characteristics and modified mechanical behaviours can be achieved.
- The chemical modification of the fiberforming polymers before fiber spinning or of the finished fibers, such as by reaction

with formaldehyde, with unsaturated aldehydes, with chlorides of aliphatic acids and others. By these treatments improvements in thermal atability and in stress-strain properties can be achieved.

3. The Development of New Fiber Forming Polymers

..

After this listing of the principles of physical and chemical modifications of conventional synthetic fibers I like to outline shortly to you the trend in the development of new fiber-forming polymers.

Hermann Staudinger, the founder of polymer chemistry expressed at the opening speech for the First World Congress of Man-made Fibers in 1954 in Paris his belief in the potential of man-made fiber developments as follows:

"It is to be expected that the nearly unlimited possibilities in variations of combining small molecules to long chain-like polymers will lead in the future to new fiber types, which will approach one day the ideal closer than nature".

This future image of a world-wide known scientist is from a pure scientific point surely right. The search for new fiber-forming polymers will indeed never cease. The drive for synthetic fibers with the ideal combination of properties for textile and other end uses will always be persued. However, one has to be aware of the fact that such efforts will meet technical problems and rise economic questions. From a technical point of view it

-30-

could for example well be that in the course of efforts for a better water absorbing synthetic fiber we may have to realize that achieving such goal will call for sacrifices with respect to other highly regarded properties, such as the excellent crease resistance and crease recovery properties, the good dimensional stability and the high wet strength of the today's synthetic fibers. Such desirable properties are actually resulting from the fact that for polyesters or polyacrylics the intermolecular bonds are not affected by absorbed water, as this is the case in cotton or other cellulosic fibers. Furthermore, a new synthetic fiber must nowadays be extremely superior over existing fiber types and having properties securing large volume application in order to cause the man-made fiber industry to consider investment of money to build the today necessary large production capacities. The efforts for new fiber-forming polymers in the past and today are more directed towards "engineering" polymers giving fibers specially suited for certain large volume end uses rather than towards the goal of the universal ideal fiber.

 $\left($

,

 \blacksquare

One of the first attempts along this "fiber engineering" line was the development of polymers giving fibers with rubber-elastic properties today known under the generic term "Spandex Fibers". In their development use was made of the basic knowledge about the principles of rubber elasticity leading to the concept of building block polymers out of flexible molecule segments, such as polyethylene oxides, and of rigid and good cristallizzble molecule segments, such as stiff aromatic isocyanates, realized in the early $1960'$ s by Du Pont chemists. Fibers made out of

 $-31 -$

- 30 -

polymers of such structure are today known as "Lycra" of Du Pont or "Dor last an" of Bayer (cf. the following figure Ne. 18 *}.*

сн_{з н} n Gummielastisches Potymeres (Lycra) •

It is worthwhile to mention in this connection the socalled "Anim-8" -fiber by the American Rohm & Haas Company. This rubber elastic fiber is made from a mixture of two polymers; one constituting the rigid and good cristallizable part composed mainly acrylonitrile copolymerized with smaller portions of ethylacrylate and methylolacrylamide, the secordone being the soft and flexible part being composed of mainly ethylacrylate copolymerized with smaller portions of acrylonitrile and methylolacrylamide. Both copolymers most probably have block polymer structure. They are produced separately using emulsion polymerization technique, being mixed together in latex form and coagulated thereafter. The copolymer mixture is spun from dimethylformamide solution by a wet spinning process. The fiber is "vulcanized" before stretching by crosslinking through the methylol functions of the methylacrylamide portion of the copolymers.

 \blacksquare

Another field of polymer development aims for fibers with more silk-like characteristics. One of these developments is the new

- 31 -

polyamide fiber "Quiana" developed a few years ago by Du Pont. The polymer used in the manufacture of this fiber is synthesized from 4,4'-diaminodicyclohexyl methane and dicarboxylic acid with $8 - 14$ carbon atoms (cf. the following figure No. 19).

 $n = 8$ $^{\circ}$ is 12

e

-33-

 $Poly-(4, 4'-diamino digyclohexyl method - dicarbon$ säure)-amid.

"Quiana"^(R)

 $\mathbf f$

,

 \blacksquare

The alicyclic molecule segment is responsible for stiffening the chain molecule resulting in a second order transition temperature above 100[°] C. This high second order transition point give rise to the excellent laundering and easy care characteristic of fabrics made from "Quiana" fibers.

A complete different route was taken in a similar effort by Toyobo Company of Japan. They developed a silk-like fiber from a graft copolymer consisting of casein with approximately 200 $%$ added-on polyacrylonitrile graft chains. This copolymer shows good water absorption compared with pure polyacrylonitrile. The casein-acrylonitrile copolymer fiber is marketed by Toyobo Company under the trade name "Chinon".

A third development along this line is the "Cordelan"-fiber of the Japanese Koijin Company. It is based on a copolymer made from vinylchloride and polyvinylalcohol most probably having graft copolymer structure. The fiber having a high halogen content is non-flammable and presently has achieved good market acception for the manufacture of non-flammable textiles.

- 33 -

Another development line in the synthetic fiber industry concerns the creation of fibers with latent crimp properties. The concept fellowed. in these efforts is in most cases based on the combination of polymers of different cristallization, heat shrinkage or swelling behaviour in socalled "bicomponent fibers". The combination of the two polymers in one fiber can either be "skin-core" type or "side by side" type as illustrated in the following figure No. 20) •

 \bullet

•

'

Querschnittstruktur latent kräuselfähiger Bikomponentenfasern

links: Kern-Mantelstruktur rechts: Paralell-C"side-by-side'') struktur

D Polymei 1 .f:ZJ Polymer 2

The two polymers can either be different in their overage molecular weight or different in their chemical structure, such as copolyester amide as one partner and copolyamideester as the second partner - just to name one of uncountable possibilities. Bicomponent fibers already on the market are "Orlon Saye lle" of Du Pont based on the use of two polyacrylonitrile polymers differing in molecular weight and composition and the "Cantrece" polyamide bicomponent fiber also marketed by Du Pont. Due to the structure difference of the two components these bicomponent fibers can be easily texturized by thermal treatment or by treatment with swelling agents during fiber manufacturing.

A good portion of the development efforts for novel fiberforming polymers today aims for high-temperature resistant and high-modulus polymer fibers. The structure principle used generally in these efforts is based on the experience that the regular incorporation of rigid structures such as aromatic rings into the polymer interlinked by direct bond from ring to ring or by small atomic groups, such as methylene groups, lead to stiffening of the structure, to high cristallization tendency and high melting or decomposition temperatures.

.
ا **و** ا

 $\mathbf f$

 \blacksquare

It would lead too far and beyond the scope of this paper to discuss in details the various structures under study. I will limit myself to mention some examples of successful new polymer developments, which are already used for the production of high temperature resistant fibers.

-35-.

--·~

The first commercially produced high temperature resistant fiber is the "Nomex" -fiber of Du Pont. The basis for this polyamide fiber is the polymer formed by polycondensation of isophthalic acid and m-phenylendiamine (cf. the following figure No. 21).

A further development was reached by Du Pont with its socalled "Fiber B" made from the polycondensate of p-aminobenzoic acid resulting in the poly-p-amino benzoic acid amide, as you can see from the following figure No. 22.

•·

 \blacksquare

l ,

This fiber is presently under testing as a new tire cord fiber.

-36-

Another example for a high-temperature resistant fiber is the "Kermel" fiber developed by Rhone-Houlenc Textiles of France, which is an aromatic polyimidamide of the structure shown in the following figure No. 23.

"Kermel"[®]

 \blacktriangledown

r

In addition to condensed ring systems highly crosslinked structure can also lead to high-temperature stable polymer products. Examples for this concept are the "Kynol" fiber developed by the American Carborundum Company based on highly crosslinked polyphenol (cf. the following figure No. 24).

 $-37-$

 $-36 -$

and the "Enkatherm" fiber of the AKZO-group which is a crosslinked metal chelate of poly-(terephthaloyl-oxalic acid-bis amidrazon) as you can see from the following figure No. 25 :

Chelatvernetztes Poly-Cterephthaloyl-oxalsäure-bis-amidrazon) 'Enkatherm"⁽⁸⁾

With this sketchy survey I hope to have given you some inside of what is going on with respect to future developments in the man-made fiber industry. I like to close my remarks with the following statement: With the development described to you in the last fifteen minutes of my paper the "third generation" in man-made fiber developments has begun. However, most experts agree that inside the next twenty years it seems unlikely that a completely new class of synthetic fibers will result and gain equal importance than the already existing polyamides, polyesters, polyacrylics or polyolefines.

