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STRUCTURE AND PROPERTIES OF FIBRES*

by

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The industrial development of a country nowadays begins with import of technology from industrialised countries.

In many cases foreign companies start production on an certain technological level. Production of a product for instance centomobiles or fibres is the first step for technological development.

With the introduction of new sophisticated technology a certain dependence arises as normally the countries are not prepared for own further development.

The reason is, that the development of technology needs own research- and development centres with a close cooperation between industry, research centres and universites.

I shall come back to this aspect at the end of my paper.

For the development of fibres to their present level of properties it was important to find out the correlation between structure and properties of fibre polymers.

In my paper I want to show to you how it was possible to create a large number of synthetic fibres with broad spectra of properties. You also know that the big four classical synthetic fibres are products which are produces in a quantity of millions of tons.



Following the order as they were invented this products are

- Polyamide 66 as a result of one decade of research work by William Hume Carothers at Du Pont
- Polyamide 6 was invented by Paul Schlack who found the acid catalysed ring opening polymerisation of caprolactum.

Polyethyleneterephthalate

was invented by I.R. Winfield at the small Company Calico Printers in 1940 and it was further on developed by IC1.

Polyacrylonitrile

as a polymer was known since forty years till in 1934 H.Rein from Cassella found a solvent for PAC, the dimethyl-formamide. But it lastet till 1941 that PACfibres from DMF have been succesfully spun by Du Pont.

For all the raw chemicals processes have been developed in a technical scale for fibres this means millions of tons per year.

We can state here the first specific demands for fibre polymers.

- 1. Fibre polymers and their raw materials are mass products
- as we learned from PAC the beste fibre polymer with the best properties is useless if we cannot spin fibres from it in one of the known spinning processes.

From todays point of view we can see four important steps in fibre development.

Step 1 The empirical chemical synthesis of linear polymers, which probably can be used for fibre spinning. From this periode the classical fibre polymers PA 66, PA 6, PES and PAC result. Parallel to the development of technical processes of the polymers much development work on the different spinningmethods has been done,

for meltspinnig, dry spinning and wetspinning.

The last two spinning processes had already been introduced in principle for the production of viscose fibres and cellulos: acetate fibres.

Step 2 In the development laboratories of the fibre producers and in research institutions intensive studies started to find correlations between molecular structure, polymer morphology and physical properties. This work is not completed even today.

> From this studies we have our knowledge on form of polymermolecules in solution and solidistate. In this periode the different models on fibre structure have been developed.

At the same time this new fibres were offered to the textile industry - and in this industry the specific processing methods of textile technology have been developed further.

We understand that this offer of new textil raw materials gave a strong impulse for the development of new machines for the production of textiles, of new dyestuffs, textile finishing products and dyeing procedures.

We can state at this point a further demand on a synthetic fibre material. "The best fibre material is useless in textiles if it cannot be dyed in all colours."

In this periode of development it was necessary to answer many questions, for instance

"How can this new fibres be processed?" "Which new processing technologies are necessary and possible - here we think only on texturising processes. "What are optimated dyeing conditions?" "How can we vary dyeing behaviour?"

Questions and questions, which for a long time. have been asked by textile industry.

To say it in one sentence the textile and fibre industry needed some decades only to show the quality and advantages of the classical synthetic

People learned the whole spectrum of properties of synthetic fibres.

Step 3 With growing understanding of the properties of synthetic fibres new demands arose which as a sum of wishes have been demanded by industry in form of profiles of demand.

fibres in its full extent.

For every specialist it is no question that we cannot combine all properties.

Nevertheless many of the profiles of demands could be realised - for instance polyamides for differential dyeing processes.

With this level of knowledge on the correlation on structure and properties many profiles of demands could be realised. This lead to a broad variety of fibres, for instance polyestercotton-types, polyester-wool-types, carrierfree dyeing polyester, polyester-tire-cord and many others.

We can state,

"the chemical and physical modification of fibres was the work of decades of fibre development."

Step 4

By chemical and physical medification of fibres almost every profile of demands could be realised. The next step was, where are the amitations. Here we discuss only two mechanical properties -

- a) extremely high modulus or
- b) high rubber elasticity.

Our knowledge on correlation of polymer structure and fibre properties showed to us the way for research work.

Of course we had to find solutions for many problems of preparative macromolecular chemistry realisation of specific structures spinning technology optimated end use and so on.

You know the result as Aramides and Elasthanes.

We shall come back to this point at the end of my lecture.

I want to show you now why a certain development took place and at which state of development we are nowadays.

Let us start with some questions on polyamide 66

"Why was this the first synthetic fibre polyamide?"



Both chemical raw materials adipic acid and hexamethylendiamin could be synthesised in a laboratory and later on in a technical scale. The polycondensation process is without serious problems. The melting point of the polymer is low enough for fibre spinning and high enough for practical use in textiles and the glastransition point is low enough for simple dyeing procedures.

When DuPont worldwide applied its patents on polyamide 66, of course many other competitors wanted equivalent fibres.



PA 6, Paul Schlack 1939

So Paul Schlack succeded in polymerisation of caprolactum.

With this two polyamides we can discuss the importance of symmetry of molecules for the macroscopie properties.

One important property for practical use is the melting point.

$$\Delta G = \Delta H - T_{S} \Delta S$$

$$\Delta G = 0$$

$$T_{S} = \frac{\Delta H}{\Delta S} \qquad \qquad \frac{\text{Enthalpy}}{\text{Entropy}}$$

At the melting temperature we have an equilibrium between solid state and melted state.

This means that changes in Gibb's Energy is zero and from this we see that the melting point T_s is the ratio between enthalpy and entropy. Entropy is a measure of order for a system, - order on the other side is a question of symmetry, this means, systems with higher symmetry ar able to have a higher order and therefore change of entropy ΔS under comparable conditions is small.



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As a consequence for PA6 and PA66 this means:

If we take tow parallel polymerchains in such a way that we can get a maximum of interaction, this is realised by dipole-dipole interactions of hydrogenbonds, we can see, that for PA6 molecules we need a certain direction for a maximum of hydrogenbonds.

In PA66 we need no high order of molecule directions, this molecule has a higher symmetry as PA6 and so a lower change in entropy at melting equilibrium and therefore a higher melting point.

Till now we have seen tow factors which determine the properties of a polymer.

- 1. molecule interaction
- 2. molecule symmetry.

With the example of Polyamide and Polyester we shall now discuss the influence of mobility of conformations of polymer chains on melting behaviour.



If we compare polyesters and polyamides of similar conformational mobility we find that polyesters have a lower melting point. The reason is, that a dipole-dipole-interaction of a polyester is lower than the interaction of carbonamide groups which form hydrogen bonds. This is the reason why Carothers besides all his efforts in synthesis of aliphatic polyesters could not get a high melting fibre forming product.



In the following slide we can see in which extent the melting point is infuenced by conformation and molecule interaction.

We also can see that under this aspect Polyethyleneterepthalate is the polyester of choice. This is the case not at least by the availability of the chemical raw materials.



An other diole for polyester is the hydrogenation product from DMT, the Cyclohexyl-dimethanole. Condensation of this product with terephthalic acid forms the cycloaliphatic polyester. To study the influence of the conformational stability on thermal properties, we have to compare with the polyester from TPA and hexenediole. We see here that conformational more rigid molecules have higher melting points.

The melting point of a polymer which can be used for fibres is <u>only one</u> of the important properties.

We can summarise a number of properties which are important for fibre polymers and fibres

Demands on the Polymer

1.

Availability of raw materials in big scale Simple polycondensation processes Low meltviscosity near melting point High productivity in spinning processes Demands on fibres

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Processing possibility on conventional textile machines Possibility for modification of fibre configuration (texturising processes) Dyeability Mechanical-, thermal- and lightstability Good mechanical properties as modulus, mechanical fastness, abrasior.#tability

Properties for use: Comfort of clothing Comfort of cleaning, washing

This are only a few of the demands we can ask for.

We cannot realise all possible demands in one fibre type. For this reason we shall produce for a long time onwards the classical synthetic fibres, but we shall optimate specific fibre properties by polymer- and fibre modification.

$$H + HN - + CH_{26} + NH - CO + CH_{24} + CO + OH PA 66$$

 $H - + HN - + CH_{25} + CO - + OH PA 6$

$$H + 0 - CH - CH - 0 - CO - CO + OH PES$$

2.

Till now we discussed systems of the polycondensation type.

We can now ask, which fibre forming polymers and of course also which monomers are available in technical scale.



From the vinyl-polymers the PVC and PAC have been long known polymers before they have been used for fibres. PAC is long known, but only new s solvents as DMF or DMA allowed spinning of PAC-fibres.

For this purpose some modifications of the polymers were necessary to improve plasticity and dyeability. This can be done by introduction of plasticising monomers as acrylates and acidic groups by copolymerisation with styrene sulfonate.

Further studies on correlation of structure and properties showed principles by which specific properties can be achieved.

Flame retardant PAC-fibres for instance can be produced from a copolymer of acrylonitrile and vinylchloride.



To understand what are the best compositions it was necessary to study the chemical reactions during pyrolysis and burning. The fast cyclisation of the nitrile groups to the first steps of carbon fibres reduces the formation of volatile burning compounds.

At this and many other examples we can demonstrate by which way demanded properties can be realised.

In every case it is necessary to understand all physical and chemical reactions which occur under certain conditions before we are able to optimate specific properties.

For the classical synthetic fibres such properties are:

force-elongation behaviour dyeability lightfastness washability flame retardancy

and many other properties.

Raw material for acrylonitrile to day is propylene. Of course polypropylene has been developed to a fibre forming polymer. But this only was possible when Ziegler and Natta had discovered the sterospecific polymerisation.



To achieve a sufficient interaction of molecule groupes and to achieve a certain conformative stiffness an isotactic arrangement of methylgroups along the polymethylen backbone is necessary.

1

Because of stereochmical and energetic reasons a polypropylene chain is arranged in a helix. The arrangement of the substituents in 1,3-position by steric reasons hinders an all-trans conformation. The system prefers a helix conformation. The polymer backbone for ral, the substituents are arranged at the outer side of the spiral. I de picture we can see this in a projection on the molecule axis.

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This helical structures under each others develop interactions in form of dispersion forces.

In isotactic polypropylene we have a structure of high order. The stiff helix is a consequence of a uniform configuration of the molecule. This reflects in the force elongation behaviour. In polypropylene we have no groups with affinity to dyestuffs. For the mechanical and thermal properties the high symmetry is important. All trials to cooperate comonomers with groups of high affinity to dyestuffs had to fail. Every change in polarity of the monomers reduces the stereospecifily of the polymerisation reaction.



Atactic poly acrylonitrile

In the radical incluced polymerisation of acrylonitrile only atactic polymers are formed. In a perspective projection with an all trans conformation of the backbone we have an irregular arrangement of the nitrile groups.

The dipule-dipole-interaction of the nitrile groups is extremely strong. This is one of the reasons for low solubility of PAC. The dipole-dipole interaction can only be lowered by strong polar solvents (DMF,DMA etc.), protonating agents as nitric acid or complexation with zinchloride.



PAC - helix interaction

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Of course also from this atactic arrangement of substituents there arises a strong dipole interaction of the nitrile groups, but this does no reach its possible maximum value.

From what I have discussed till now we can conclude:

"Symmetry and configuration of a polymer group deteramine the polymer conformation. The molecule conformation determines the arrangement of the chain molecules in the crystalline and non crystalline part of the polymer.

In the noncrystalline part we have a chain segment mobility under changes of conformation."

chemical constitution		configuration
configuration molecular interaction}	-	conformation
conformation		microstructure
microstructure		crystallites
		secondary structure
		tertiery structure

MACROSCOPIC PROPERTIES

The most probable conformation of a molecule is determined by the configuration which results from chemical structure.

Conformation but also determines structure units which determine secondary structure.

Macroscopic properties as mechanical fastness and modulus we can only measure at solids of macroscopie dimensions.

This means we have to observe the arrangment of ensembles of molecules if we want to discuss modulus elasticity and so on.

At this point we come to the question:

What is our picture of the arrangement of the molecules in the polymer? This means, we have to construct structural models and proof this models by physical measuring methods, x-ray-structure etc. or we have to deviate this structural models from physical measurements.

From x-ray analysis we know that the polymers are only partly crystalline.

If we realise what is the difference in the way of crystallisation of a chain molecule to the way of crystallization of a low molecular substance, then we can understand our present structural model.



In low molecular compounds the free places of a lattice are filled one after the other and indepent from each other.



An other situation we have with high molecular compounds. Here the segments of a macromolecule is built in different crystallites at the same time.

In the crystalline parts we find a strong interaction of the polymer chains.



Fig. 2. String model of the fringed micelle concept.

A very instructive model of a fibre structure has been given by W. Statton.

In the noncrystelline areas the molecules above the glass transition point move against each others, this means we have a certain chain segment mobility.

The chain segment mobility becomes higher in the presence of water, carriers, softeners etc. With this mobility we get a dynamic movement of the free volume which allows a dyestuffmolecule to diffuse into the polyme⁻.

From this structure model we can draw conclusions for further developments in the fibre field.

In polyethyleneterephthalate the glass transition point is above 100°C - this means in an open dyebath the chain segment mobility of polyester is to low for a sufficient diffusion velocity of substances which have chain segment mobilities as for instance carriers.

A higher chain segment mobility results from commonomers with low conformational stiffness. For this reason we can form fibres from a copolycondensate of ethyleneglycol, polyethylenglycol and terephthalic acid which can be dyed in an open dyebath.

With the realisation of a carrierfree devable polyester we have seen, how a straight foreward modification of properties is possible.

We come now to discuss the last and latest aspect of fibre development - the definite construction of fibre properties.

To understand this development we look again on three possible structure models of polymers and ask which macroscopic properties result from such structures.





In a structure model of a classical two phase system we have long periodes of 100-200 Å length. The amorphous and crystalline part have the same chemical constitution. The glass transition point is about 30-100°C, dependent upon the conditions. This means for dyeing we need temperatures from 40-130°C.

If we want a fibre with high rubber elasticity we need segmented polymers. In this systems we have a sequence of segments with low and high molecule interaction.

For realisation of such structures we can use a principle which was discovered in 1935 by O. Bayer, the di-isocyanate-poly-addition-principe. Segments with high hydrogenbond-density form the socalled hard blocks and form points of physical crosslinking.

Polyether-parts in the polymer have a high conformative mobility and a very low glass transition point.

This segments at room temperature are in a quasi-liquid state.

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An other type of polymers which can be used for production of fibres consists of conformative extremly stiff polymerchains with a high interaction of the polymer chains.

We have already seen to which extent thermal and thermomechanical properties are determined by molecule conformation.

If we apply this principle on polyamides we can expect that aromatic polyamides will have specific thermomechanical properties.



As monomers we have here p-amino-bencoic acid, terepthalic acid, isophthalic acid, p- or m-phenylendiamine.

For the production of fibre forming polycondensates we have as a general rule.

ilonomer and polymer should be over the whole polycondensation process in an homogeneous state.

Polymers from the meantioned monomers however melt above 400-600°C. For this reason we cannot use a melt polycondensation process. It is necessary to condensate a solution-polycondensation process. In addition the amino-groups of the aromatic compounds have a low reactivity so that we have to activate the carbonic acid inform of their acid chlorides.



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For this reason we add dicarbonic acid chlorides to a solution of aromatic diamines in an apmic polar solvent, which in its anhydrous form is a strong base to add the developed hydrogen chloride.

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Polymers of this typ form physically crosslinks which leads to a low segment mobility. The result is a very high melting point.



If we succeded in synthesis of a polymer of sufficient high molecular weight, and as we cannot use a meltspinning process -, we need a solvent to spin the polymers to fibres.

Poly-m-phenylene-isophthalamide is soluble in dimethyl-acetamide lithiumchloride. By addition of the lithiumchloride to the carbonamide bond a polyelectrolyte is formed which is soluble in the solvent DMA.

From such a solution we can spin fibres. The fibre porperties are those of a relative stiff fibre. But as we have only a low concentration of carbonhydrogen-bonds in the polymer we have a low flammability.



For this reason textile materials from this fibres are used for professional clothing where a danger of fire is possible.

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arientation of hydrogen-bands in paly-p-phenylene-t-trephilhalamide

By polycondensation of p-phenylendiamine and terephthalatic acid chloride we get the p-linked polyamide. Here also we have a crosslinked hydrogenbond system. In this system the symmetry is still higher than in the meta-linked system.

Such polymersystems dissolve in sulfuric acid. The carbonamide groups are protonated and the resulting polyelectrolyte forms anisotropic solutions of liquid crystals. This leads to a high preorientation of the molecules before spinning.



t_s + 375* 172g/dtex

orientation of hydrogen-bond-dipoles

The thermal behaviour, modulus and strength of fibres is determined by symmetry of the polymergroups and by order and orientation.

In which way the fibre modulus is influenced by symmetry and hydrogenbond-direction we see in a comparison of some aramide structures.

The higher the symmetry of the system and the lower the inner energy by dipole compensation the higher we find the modulus and melting point.

which consequences can we draw from this facts on the use of aramides.

	aliphatic PA	Poly-m-phenylene isophthatomide	glass	Poly-p-phenylene 'arephtholomide	steel	carbon
tensile strength [kg/mm²]	185	95	350	427	420	350
modulus [kg/mm²]	9019	2503	10019	19055	21000	45000
density [g/cm³]	143	1.40	2 58	145	7.9	1.7
specific tensile strength [km]	130	67.8	1356	2945	532	205
specific modulus [km]	6306	1781	3883	[]]14]	2658	26500

Fibres with a high modulus are important components for composites.

If we compare the moduli of glass-, steel-, carbon- and aramides fibres, we see that this data are on the same level.

For many uses however not only tensile strength and modulus are important but reenforcing strength, this means tensile strength and modulus per weight of the fibre.

For this reason we have to take into our calculation the density of the material, this means, we have to express the reenforcing power of the fibre in from of a specific fastness or specific modulus.

Because of the low density we find for poly-p-phenylenterephthalamide extremiy high specific tensile strength and modulus. If we take also into consideration the price we get with this fibre the highest value per money unit. Besides this no other fibre has such a high dynamic modulus. So we can use this for tire cord or antiballistic clothing.

Of course such a differentiation is only very coarse, as every specific fibre owns further spcific properties which determine their application.



We know from the spectrum of PA66 that this fibre is especially useful for textiles.

For thermal resistance however a sufficient thermal resistance of shape is necessary which is connected with the melting point and glass-transition point. In PA56 we have a sufficient low thermoplasticity so that we are able to texturise. Dyeability is favoured by the low glass transition point in the presence of water in a dyeing bath. From the high symmetric, p-connected aramides we use the high staticand dynamic modulus. Such a high modulus prevents the use in textiles for clothing. Systems with lower symmetry as poly-m-phenylene-isophthalate have a low flammability. The reason is the low percentage of C-H-bonds. So this system can be used for special clothing.

A still higher thermal stability is achieved if we lower the percentage of C-H-bonds further by using poly-heterocycles. This we find in the poly-benz-imidazole.

In Polyheterocycles and condensed aromatic systems temperature fastness is on a still higher level. But also here we have to make compromises between bending-behaviour, compressibility, fastness vertical to the fibre axis on the one side and modulus and temperature resultance on the other side.



Elasthane fibre polymers

We have seen in the last chapter how the density of energy of cohesion of a linear polymere is influencing the macroscopic fibre properties.

An other building-principle of polymers consists in the arrangement of a polymer in segments of different energy of molecule interaction.

A rather defined arrangement of building blocks is only possible in stepwise synthesis of the polymer.



classical crystalline-amorphous system



For this purpose we can connect segments of low molecule interactions and high conformational mobility - for instance polyethers - with segments of high potential hydrogenbond density.

If we arrange two building blocks of this type in an alternating segquence we can realise a entropy-elastic fibre forming polymer. The soft segments at room temperature are in a liquid state.



If we give a load on a fibre system of this type, under the most favorable conditions all polyethersegments come to an all-trans-conformation. The hard blocks stay crosslinked because of their high hydrogenbridge density. If we lower the load for on such a fibre, the polyethers will come to a state of higher entropy. This behaviour is reflected in the properties of a rubber elastic material. By the discussed principle of syntheses we can realise systems with a reversible elongation of 700%.

But what is the difference compared with normal classical rubber material?

Rubber elasticity of natural and synthetic rubber results only from a vulcanisation process. The formed covalent crosslinks lead to a polymer which is not soluble in any solvent. So we cannot produce fibres of the necessary low titer.

In the polyurethanes however we have no covalent bonds between the chain molucules, but only hydrogen bonds. For this reason this polymers disolve in polar solvents and from such polymer solutions we can spin elastomer fibres.

If we spin around such elastomer yarns PA6 or PA66 we can get highly elastic core yarns for elastic textiles.



We have now discussed the most important principles of fibre polymer construction.

For most applications modulus and maximum elongation is important. With the present knowledge on correlation of structure and properties we can realise different fibre types with elongations of 1-700% and with moduli from 0, 2 - 1000 g/dtex.

We have also discussed the question - how interaction of polymer building groups determine fibre properties.

The used momers determine the chemical constitution of the polymer - its chemical properties.

The basic chemical units determine the configuration of the polymer, the interaction of the building determine stereochemistry, conformation, crystallisation and all cooperative properties.

The thermal behaviour, meltviscosity, solubility etc. determine the possibility to spin fibres.

Spin- and stretching processes at last determine morphology and possibility to optimate enherent properties.

Out of this interdependence of chemical, physical and morphological structure at last there results a profile of properties.

mechanical properties	tensile strength,modulus,relaxation abrasion resistance
textile properties	hand, bendingmodulus, stiffness surface structure light reflection appearance, drape
comfort properties	water uptake,water transport thermal insulation,wearing comfort comfort of washing,drycleaning non ironing
textile chemical properties	bleaching,opt. brightening. dyeing textile_chemical_modification
	antistatic , soil release flame retardent , crease resistance

If we can use o fibre polymere in textile technology or not, is a question of the level of the sum of fibre properties.

This properties are:

mechanical properties	35	fastness, modulus, relacation behaviour abrosion restistance etc.
textile properties	as	hand, bending modulus stiffness, surface structure light reflection appearance, esthetics etc.

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comfort of clothing thermal insulation water transport physiological properties cleaning comfort as washing dry cleaning etc.

To realise all this properties we need a number of chemical and technological processes.

It is one of the most important conditions, that the fibres can be processed in pure form or in blends with natural fibres on conventional textile machinery.

But also an other group of demands to produce textiles from fibres have to be fulfilled.

For instance a number of textile chemical processes have to be applicable, such as dyeing, bleaching, textile chemical modifications for soil release, antistatics, shrink proofing, flame retardancy and many others.

We cannot realise these properties on a textile material without understanding the behaviour of fibres in the textile manufacturing processes.

We now also understand that it is not possible to have one universal fibre.

The raw materials we use nowadays in fibre and textile-production allow to realise a broad variety of properties.

The demand on the specific properties changes nowadays very rapidly. The fibre industry has to give offers on the demands of the textile industry. This is only possible if modifications in the production processes are made.

However, before modifications in the production processes are made, material properties as a function of chemical, physical- and processmodifications have to be evaluated.

For this purpose the research and development infra structure must be available.

De elopment infrastructure however consist of a certain hardware, as institutes, buildings equipment etc., however also of people, scientists, technicians etc., who can do the necessary work. The establishment of research teams in the fields of applied oriented fundamental research needs many years of continous support.

MONOMER	PETROCHEM, INDUSTRY
POLYMER	FIBRE INDUSTRY
FIBRE	FIBRE INDUSTRY
YARN	TEXTILE INDUSTRY
WEAVING	TEXTILE INDUSTRY
KNITTING	TEXTILE INDUSTRY
DYEING	TEXTILE FINISHING INDUSTRY
PRINTING	TEXTILE FINISHING INDUSTRY

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TAILORING	CLOTHING	INDUSTRY
CONSUMER		

ENGINEERING APPLICATION

MACHINE CONSTRUCTION &

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PROCESS TECHNOLOGY

PROCESS	DEVELOPMENT
DYESTUFF	DEVELOPMENT
MACHINE	CONSTRUCTION

DESIGN

WASHING

DRY CLEANING

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FLOW OF RECOMMENDATIONS

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FIBRE PRODUCER DEVELOPMENT OF FIBRE TYPES

< RECOMMENDATIONS FOR PROCESSING OF

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FIBRES >

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TEXTILE INDUSTRY

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FIBRE TO YARN PROCESSING TEXTURISING WEAVING KNITTING

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TEXTILE FINISHING INDUSTRY

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DYEING

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PRINTING

TEXTILE FINISHING

DYESTUFF INDUSTRY

<u>APPLICATION SERVICE</u>

RECOMMENDATIONS FOR

DYEING, PRINTING ETC.

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DYESTUFF INDUSTRY

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DEVELOPMENT OF DYESTUFFS TEXTILE FINISHING AIDS TEXTILE FINISHING PROCESSES RECOMMENDATIONS FOR APPLICATION

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CONTRACTS ADVISERY SERVICES

RESEARCH







ADVISERY SERVICES

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