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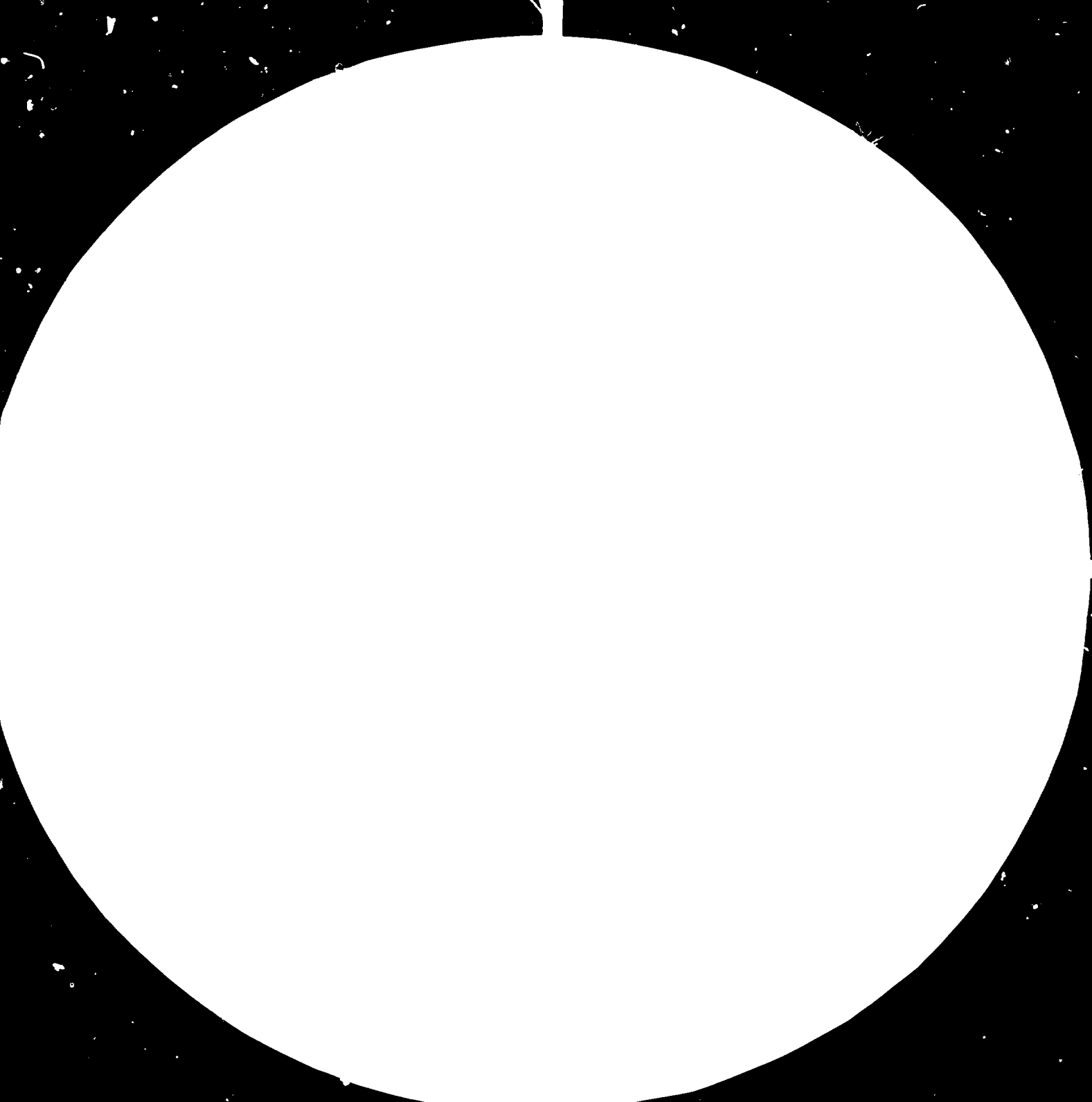

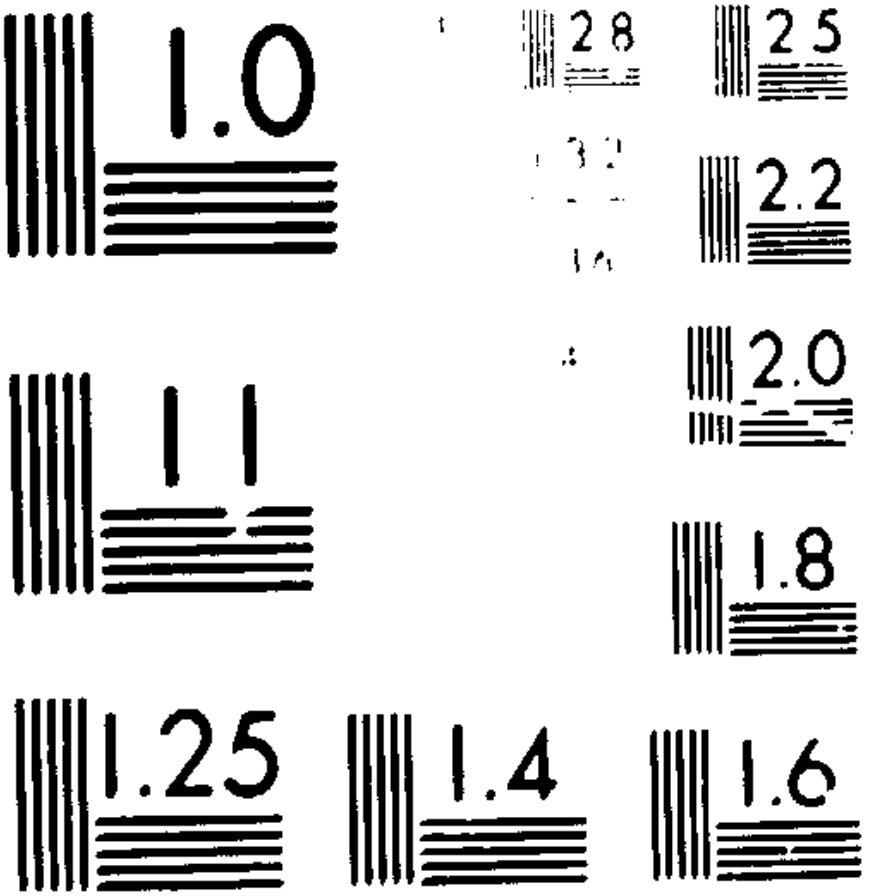
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CHEMICAL METHODS OF FIBRE MODIFICATION

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CHEMICAL METHODS OF FIBRE MODIFICATION

It is almost forty years ago that the first attempts were made to improve the behaviour of textiles composed of natural and regenerated cellulose fibres by means of a chemical modification. The problem was not studied very intensively at that time, however, because the end consumer, having no basis for comparison, did not show any particular interest in having things improved. The situation changed drastically, however, with the development of synthetic textiles in the first postwar years. Fabrics composed of these new fibres required no ironing after washing, and they did not shrink or stretch when laundered under the prescribed conditions. The end consumer soon learnt to appreciate the advantages of these new textile and began to demand a similar behaviour from cellulosic textiles.

Because of the big development of synthetic fibres there are made various methods in the last years for a chemical modification of these fibres.

This large area of chemical modified fibres should be shown in the following.

CHEMICAL MODIFICATION VIA CROSSLINKING REACTIONS FOR CELLULOSIC FIBRES

Properties of cellulose fibres:

1) high water absorption, the ability to transport moisture, and the associated good wearing characteristics are advantages, and
2) high shrinkage and poor crease recovery are disadvantages.

The disadvantages of cellulose can be reduced by chemical modification, and this can be done without affecting the advantages to any significant extent.

The chemical modification of cellulosic textiles is a development that became inevitable, particularly in the last twenty years, in view of the growing significance of synthetic fibres. Since textile materials made of synthetic fibres are generally outstandingly crease-resistant and easy to look after, demands began to be made that cellulosic fibre textiles should have the same properties. These demands by the market caused the chemical industry to carry out extensive development work, the result of which was a large number of chemically highly varied products for the resin-finishing of cellulose.

In principle, there are two fundamentally different methods of finishing cellulose with chemicals. The first method consists of depositing a low-molecular-weight chemical by polycondensation in the form of a high-molecular-weight elastic synthetic resin on the fibre. This involves no formation, or hardly any formation, of bonds between the resin and the fibre. The second method uses a chemical that does not undergo polycondensation. This chemical is made to react with the cellulose, resulting in its modification. In this reaction, the reactive groups of the crosslinking agent form crosslinkages with the hydroxyl groups of the cellulose, with formation of stable atomic bonds between different cellulose molecules. In fact, though, both kinds of reaction may occur together. The resin-finishing chemicals can be subdivided into "self-crosslinking agents" and "reactant types", depending on which of the two reactions predominates in the condensation reaction.

Crosslinking of cellulose restricts the possibility of the chain molecules being displaced. The highly valued properties, such as crease-recovery and dimensional stability, are improved according to the degree of crosslinking. At the same time, the extensibility of the fibre is diminished to a greater or less degree. This becomes evident in the fibres becoming somewhat more brittle with a consequent loss in abrasion resistance, tensile strength, and tearing strength, again to a varying degree. The impairment of these properties is particularly noticeable with textile materials made of natural cellulosic fibres.

CROSSLINKING AGENTS

The first attempts to resin finish cellulose were made with formaldehyde by D. ESCHALIER, German Patent 197,965 (30.4.1908) However, it was soon found that considerably better results could be achieved if the formaldehyde were applied as a component of a system. When the first patent applications were filed by Tootal, Broadhurst and Lee over 40 years ago for shrink resist and noncrush cottons by condensation in situ of resins, such as urea-formaldehyde and phenol-formaldehyde, little was known about the molecular prccesses involved.

Now it is widely accepted that these fabric properties are achieved by cross-linking the cellulose chains through the hydroxyl groups on the glucose units. There are many agents available and they tend to be either monomeric compounds or low molecular weight polymers with two or more reactive sites. They react with the hydroxyl groups, preferably on different cellulose molecules, at elevated temperatures with the aid of catalysts, usually by a condensation mechanism. The classical procedure for their application is the pad-dry-cure process, where the drying is accomplished at around 100° C, and the curing, during which most of the crosslinking occurs, at 135-165° C.

The oldest and most important group of crosslinking agents is formed by reacting formaldehyde with diamino and diamido compounds to form diamino-and diamido- methylol adducts. These compounds are also produced by reacting formaldehyde with appropriate compounds containing NH or NH_2 groups.

These diamino- and diamidomethylol compounds react with hydroxyl groups in the presence of acidic catalysts at elevated temperatures. Free acids, such as lactic, tartaric and hydrochloric, or latent lewis acids, such as zinc nitrate and magnesium chloride, may be used. Other catalysts which have been studied and used, include zinc fluoroborate, ammonium sulfate, ammonium phosphate, and amine hydrochlorides.

The crosslinking agents include:

Picture 1 Picture 2

Other crosslinking agents include the acetats sulfone derivates and aziridine derivatives. O-methylol compounds such as the dimethylol-alkane-diols, are of less importance. To impart stability, these N-or O-methylol compounds may be etherified with methanol to produce N-or O-methoxylmethyl compounds. Other types of chemical compounds, such as sulphonium innersalts (betaines) and epichlorhydrin are used only in the wet and multi-stage crosslinking processes.

In the next picture the most important types of crosslinking agents and the processes in which they are mainly used are shown.

Picture 3.

All these compounds react with cotton fibre in the following manner:

Picture 4

The earliest reactions with urea-formaldehyde and melamine-formaldehyde resins were probably twofold with the methylol groups ($-CH_2OH$) reacting both with the cellulose, as shown above, as well as reacting with itself to yield a three dimensional resin. It is generally accepted that the desirable effects are achieved by the introduction of covalent cross-links and not by the internally deposited polymer resulting from the self-condensation reaction of the dimethylol cross-linking agent. All aspects of this question have not been resolved, but it has been shown that only a small fraction of the reagent which is added to the fibre is involved in covalent crosslinking.

The first resin finishes and crosslinking reactions changed the crease recovery angle of a cotton fabric from approximately 160° to $200-220^{\circ}$. The wash and wear era of the 1950's required angles of $230-260^{\circ}$ and the fabrics were noted for their smooth drying qualities. Now in the era of durable press, a crease recovery angle of $280-320^{\circ}$ is required. The concept of durable press is based on the application and fixation of the reactants to the fabric with curing deferred until the garment is fabricated. This transfers the crosslinking reactions from the finishing plant to the garment manufactures. Here, the appropriate creases and pleats are put in, and the garment is cured for a predetermined time and temperature.

Today there are a variety of durable-press processes divided into three groups:

1) post curing
2) pre curing
3) two stage curing

In all these processes, the chemical reactions are similar but the distribution and number of crosslinks varys. In some instances, there may be a balance achieved between crosslinks and resin formation.

In the reaction between cellulose and a variety of difunctional reagents, we can expect the reactivities of the hydroxyl groups in the C-2, C-3 and C-6 positions of the glucopyranosyl repeat unit to be influenced by the election densities at the individual oxygen atoms, the steric interferences around the hydroxyl groups, the nature of the reactant etc.

In addition to reactivities as influenced by these chemical factors, the availability of the hydroxyls in less ordered or amorphous regions and on the surface of the ordered or crystalline regions of the fibre is an important factor in the extent of chemical modification which is achieved and, therefore, in the observed changes in physical fibre and fabric properties. The accessibility of the hydroxyl groups are dependent on the nature of the reagents and the conditions under which they are applied and reacted.

The introduction of crosslinks yields a fibre with higher resilience, defined as recovery from deformation, decreased extensibility, and decreased strength. Such changes in the fibre are consistent with a decreased chain mobility which is associated with crosslinking. In fabrics these changes appear as improved wrinkle recovery and crease resistance but decreased fabric strength and abrasion resistance.

GRAFT POLYMERIZATION FOR CELLULOSIC FIBRES

Grafting of synthetic polymers to cotton is an effective method for modifying its properties. Grafting may be accomplished either by reacting a preformed polymer with the cotton or by actually causing polymerization to take place at active sites on the cotton cellulose. Reaction with preformed polymers are of limited use since diffusion of the high molecular weight synthetic polymer limits the grafting reaction to the fibre surface. The polymerization of a monomer to a cellulose chain can be accomplished by either ionic or free radical initiation methods. The redox system and high-energy radiation techniques have been extensively investigated.

Some of the redox systems which have been studied for the graft polymerization of vinyl monomers onto cellulose include cerie salts, a ferrous salt-hydrogen peroxid, pentavalent vanadium etc. The vinyl monomers which have been grafted onto cotton fibres either by a redox system or by a radiation method include the acrylonitrile, acrylates, styrene, vinyl acetate, vinyl chloride etc.

Graft polymers on cotton may be used to waterproof, improve rottresistance, flameproof, change dye characteristics, and modify physical properties, such as abrasion resistance and stiffness.

Esterification of cellulosic fibres

The technical most important derivatives of cellulose are the esters. The first place takes the acetylated cellulose with regard to the quantity. In the last years a big number of cellulose esters of other aliphatic and aromatic carboxylic-acids were examinated because of the great development of high finishing technique.

In my work I have made cellulose ester of

anhydric phthalylglutaminic acid ,and

anhydric phthalylasparaginic acid.

This reaction is shown by picture 5

In this way modified cotton fibres have a very good acid resistance, improved wrinkle recovery a large change of dyeability and a little increased flame resistance.

The tear strength decreases with the high of the reaction degree like all the modificated celluloses. A new method to form cellulose ester is the reaction of cellulose with phenolic or mercaptic esters with carboxylic acids at higher temperatures. These reactive carboxylic esters are used in the form of aqueous solutions of their alkali salts, the reaction with cellulose occuring at 170°-200° C. The reaction can take place in open apparatus.

Very interesting changes in the properties can be seen by the partial esterification of cellulose with benzoe acid or adipin acid.

Picture 6

In this way modified cellulose shows a higher rott resistance, a increasing of the wrinkle recovery and a change of dyeability (reserve against substantive dyes and high affinity to dispersion dyes).

RAYON: CHEMICAL MODIFICATION

Many of the crosslinking agents, thermosetting resins, and vinyl monomers that have been applied to cotton have also been evaluated on rayon fibres and fabrics.

The technique of crosslinking rayon fibres in a wet or swollen state has shown some interesting results: a very high wet resilience, about normal dry resilience, a high fluid-holding capacity, and a high resistance to NaOH. Its strength under standard conditions will be 10-30% lower and its elongation will be 150-190% higher than an untreated rayon.

Grafting: As stated previously, all vinyl monomers which can be grafted onto cotton can also be reacted with rayon. Grafting of compounds such as acrylonitrile or styrene-acrylonitrile onto fibres can give fabrics of high wrinkle recovery, a wool-like hand and good wash-and-wear properties.

CELLULOSE ACETAT: CHEMICAL MODIFICATION

Cellulose acetat fibres with a degree of substitution of 2,3-2,5 has a sufficient number of unreacted hydroxyl groups to allow it to undergo the typical grafting reactions of cellulose. Monomers which have been used in grafting include styrene, acrylonitrile, many acrylate and methacrylate esters, and vinyl acetate. Grafts may be obtained by free radical initiation from redox and peroxide systems or from

high energy radiation, such as γ-rays. Among the acrylate grafts and vapor phase treatment with the monomers, improved dry- and wet-crease recovery was obtained with propyl and butyl acrylate. About 5% graft gave maximum improvement in crease resistance and tear strength. The fibres also showed rubberlike elasticity and water repellency.

CHEMICAL MODIFICATION OF WOOL

The complex structure of a wool fibre presents problems in harvesting, cleaning, and processing. It has scales on its surface which cause one-directional frictional migration producing felting; it has high moisture absorption which causes swelling; and it is highly resilient and can shrink under relaxation conditions. Furthermore, in order to maintain good color and fibre physical properties, cleaning, bleaching, setting, and other treatments must be carefully controlled. Wool fabrics can be made dimensionally stable and smooth drying by proper chemical treatments to control felting shrinkage. To accomplish this, the scales on the fibre can be removed or their edges coated to the fibre surface. Relaxation shrinkage can be controlled by the introduction of crosslinks which are more stable than -s-s-bonds, by grafting or by in situ polymerization.

Aldehydes

have not proven to be useful chemicals for stabilizing wool, although formaldehyde can react with amino, amido, guanidyl, hydroxyl, phenolic, and indole groups and reduce disulfide bonds. It cannot react with two amino groups but it seems to crosslink guanidyl groups as well as an amino group and an amido group. The principal advantage observed with formaldehyde is the reduced solubility of the fibre in alkali and, fortunately, this apparent protection does

not cause any corresponding change in mechanical behavior.

Stabilization of wool is also chaimed upon treatment with glutaraldehyde in a rather long reaction cycle requiring additions of sodium carbonate to maintain pH 8.

Another method for rendering wool shrink resistant is by treating with a methyolderivative of a mono- or dihydrazide. Benzoquinone reacts with wool to form crosslinks, and although it discolors the fibre. It will react with amino and thiol groups in the following manner :

Picture 7

as well as polymerize with itself. The changes observed in the treated fibre are increased strength and a reduction in felting.

Additional reactive polymers which have been applied to wool could be described as a polyethylene type. Chlorosulfonated polyethylene is effective for shrinkage control but its use requires extensive cure times which are not practical.

However, such structures

Picture 8

can be made containing varying amounts of ethylene, methacryloylchloride, and vinylacetate. This polymer is soluble in aromatic petroleum solvents and can be applied in a normal dip, pad, and cure process. This method involves the application of preformed polymers containing reactive groups. The polymers may then be

easily crosslinked forming an ultrathin film on the fibre surface. The method avoids the need for a curing process and requires very slow solids pickup to effectively control felting shrinkage. The technique has been extended to include polyesters and polyethers to yield polymethanes. The cross-linking agent used in both cases are diamines such as ethylene-, 1,4-butane-, and hexamethylen-. The crosslinked methanes give an improvement in most physical properties with good to excellent shrink resistance, although the urethane elastomers themselves have poor solubility in aliphatic hydrocarbons.

Other polymers which are reactive and have been applied from solution are an ethylenic terpolymer containing acid chloride groups:

polyethylenimine
epichlorhydrin
polyacrylate

Considerable in situ polymerization work has been done with vinyl monomers, especially acrylonitrile and the acrylates. These compounds may be polymerized by a free-radical mechanism or in a simple ionic redox system etc. Vinyl monomers such as styrene have been polymerized in situ after radiation. When the monomer is applied first and then grafted by radiation, different water sorption properties result. These sorption properties, of course, are also influenced by the nature of the grafted polymer. An acrylamide or acrylic acid graft would not show the water sorption effects of a styrene graft.

Other in situ polymer reactions which have been considered for shrinkproofing wool include a nylon from (p-nitrophenyl) sebacate and hexamethylene diamine, diisocyanate with a diamine and polymers from aziridinyl compounds.

CHEMICAL MODIFICATION OF POLYAMIDS

N y l o n - 6 , 6

can modified by crosslinking, copolymerization and grafting.
Nylon - 6,6, because of its mono-substituted amide repeat units and its amine end groups, can be crosslinked with formaldehyde.

This modified fibres are insoluble in formic acid and resistant to melting.

X-ray examination shows that crosslinking occurs in the amorphous areas. The fibres retain good dyeability, strength, and resilience.

Nylon - 6,6 has also been reacted with diisocyanates and diacid chlorides.

Also the following reactions were examined:

-reactions of amid groups with unsaturated aldehyds
-chemical conversion of unsaturated polyamids
-modification of fibres of polyamide-blends by means of semicarbazide etc.

The obtained results prove that by chemical reactions of the polymer-chain the properties of polyamide fibres can be remarkably modified.

Modification of fibre properties can easily brought about by copolymerization. Comonomers of recent interest appear to be those which give basic dyeability to the polymer.

These includes: 5-sulfoisophthalic acid

sulfanilic acid

2,5-aniline disulfonic acid

sodium 3,5 - (methoxycarboxyl)-benzene sulfonate

2,6-disulfonates of carboxybenzene

Cyclohexylphosphonic or cyclopentylphosphonic acids, ß-aminopropylpiperazin or 5-amino-isophthalic acid have been used to give improved acid dyeability.

These reactants showspicture 9

The name for this fibres are polyamid-differential-dyeing and cross-dyeing with the varies of light-, deep-, ultra deep-types.

The next pictures show the chemical reactions: (10)

By the use of a novel resist agent (Sandospace R, Sandoz AG), which changes the affinity of polyamide fibres for acid and cationic dyestuffs, it is possible to easily obtain composite, mouliné, multicolour, print, and special effects. The product is suitable for all the usual types of polyamide fibres and is applied, depending on the desired effect, by the exhaust method, in printing, or by impregnation with subsequent steam fixation. All articles thus treated are dyed in the piece, i.e. at the end of processing, regardless of whether woven or hust fabrics or carpets are concerned.

The chemical method of this novel resist shows picture 11

Considerable research on aliphatic - aromatic polyamides has been carried out in order to improve the thermal properties that are associated with flat spotting in tires.

However, this approach has led to only limited commercial success. Other modifications include blends of nylon - 6,6 or nylon - 6 with amino acid copolymers, blends of nylon - 6 with copolymeric 6,6 containing long-chain amino alcohols and terephthalic acid for crimpable fibres, and additions of oleic acid dimer or hydroxy fatty acid or fatty acid amide for built-in lubricity.

The chemistry of grafting has been applied to polyamide fibres as to every other textile fibre and has been evaluated as a means of modifying and improving fibre properties. The properties sought range from increased hydrophilicity to increased melting point. When nylon - 6,6 is reacted with ethylene oxide to form a hydroxyethyl derivative, the ethylene oxide is present largely a chemically bonded polyethylene oxide chains and produces a flexible material with higher water sorption properties. The "hydroxyethyl nylon" retains the solubility and high-melting behavior of nylon but becomes flexible, hydrophilic, and also shows the second-order transition behavior of the polyethylene oxide chains.

In order to increase the melting of the fibre, maleic acid and acrylic acid were grafted and a change from 250 to over 350° C was obtained. Grafting may be initiated by use of hydrogen peroxide and a water-soluble formaldehyde sulfoxylate salt (Na). The acrylic acid graft is converted to the sodium salt by heating the fabric in a sodium carbonate solution and then replacing the sodium ions with calcium ions from a calcium acetate solution. The nylon-acrylic acid graft yields fabrics which have a high resistance to "hole melting". Styrene, vinylidene chloride, and methyldodeca (oxyethylene) methacrylate have been similarly grafted to nylon-6,6 using heat as the sole initiator.

Grafting may also be accomplished using high-energy sources by γ-radiation. The nylon fabric is made flame resistant by a radiation graft copolymer of vinylidene chloride and vinyl acetate. The monomers are padded on the fabric and placed in aluminium foil and then irradiated. Improved acid dyeability, reduced static biuldup, and increased soil resistance may often be obtained by grafting a vinylpyridine or an unsaturated amine.

N y l o n - 6

structures are subject to derivatization in that there are substituted amide groups, amino end groups, and carboxyl end groups. In addition, the polymers low melting point can be increased and its complex solid state structure can be stabilized by chemical methods.

One of the first chemical treatments given to synthetic polyamides is the preparation of N-methylol. N-alkoxymethyl, and N-alkylthiomethyl derivatives. These reactions are carried out with formaldehyde to yield an N-methylol derivative or with formaldehyde in the presence of an alcohol or mercaptan to yield the N-alkoxymethyl or N-alkylthiomethyl derivatives. The reaction occurs in the "amorphous region" of drawn filaments. When hydroxy-methylation of nylon-6 fibres reaches 40 wt.%, the fibres begin to adhere and these have been pressed in a heated mold to form a sheet that has good impact strength, and is microscopically porous. A possible use for this is a substitute for leather.

Picture 12

The partial substitution of amide hydrogens, as, for example, the addition of ethylene oxide, can bring about a lowering of melting point and a loss of strength - but the elasticity increases.

Picture 13

Partial benzoylation up to a degree of substitution (DS) of about 0,1 decreases the elongation and the tenacity about 60-80%.

Chemical crosslinks may be formed in nylon-6 fibres by means of adipoyl and sebacoyl acid chlorides, hexamethylen and tolylene diisocyanates, cyanuric chloride and S_2Cl_2 as well as by the synthesis of acetoacetate-polyamid derivatives which are capable of crosslinking with diketene.

In general, the elastic modulus and thermal stability increase regardless of the crosslinking agent. The most effective crosslinking agent is a diisocyanate and, in addition fibres crosslinked with these compounds either retain or else increase in breaking strength. The fibres treated with S_2Cl_2 had the greatest thermal stability.

Picture 14

The picture shows the introduction of disulfide and alkylene sulfide crosslinks. The disulfide linkage is obtained by methoxymethylation of the fibre followed by treatment with an acidic aqueous solution of thiourea and then potassium hydroxide.

Nylon-6 has also been grafted with a variety of vinyl monomers and the property changes of the fibres have been determined. Acrylonitrile grafts have received considerable study because of the possible advantages of handling acrylonitrile in a vapor phase.

The reaction may be carried out by radiation or by photochemical initiation. Other crafting reagent are styrene, acrylonitrile, vinylacetate, methylacrylate, vinylfluoride, vinylidenfluoride, trifluorochloroethylene and hexafluoropropylene.

CHEMICAL MODIFICATION OF ACRYLIC FIBRES

Wrinkle recovery, set, shrinkage, and crimp are aspects of acrylic fibres that are usually controlled by the choise of comonomer and the processing of the fibre immediately after the fibre-forming operations or after fabrication. The wrinkle recovery of a fabric can be improved by heating under constant length and width at 200-220° C for a short time.

Setting can be accomplished by the application of a swelling agent before or after the desired deformation. The use of alkylamides and cyanoalkylamides are reported to be useful in achieving this type of fibre deformation.

The modification of the fibre properties in acrylic fibres by crosslinking has been to date principally a chemical exercise. Crosslinking can be accomplished by irradiation or by incorporation of a reactive comonomer.

The comonomers which furnish potential crosslinking sites are

1) methacrolein
2) N-methylol acrylamide
3) glycidyl methacrylate
4) diketene
5) methylene bisacrylamide

The fibre property changes, which can be obtained by the introduction of crosslinks, depend on the state of the fibre at the time the crosslinks are formed. When a partially crosslinked polymer is spun into a fibre improved tear

strength, dyeability, and good elasticity are claimed. When the crosslink is formed after crimping, the crimp is fixed. Strength and elongation are usually decreased somewhat, but thermal stability is frequently increased considerably. Polyacrylic knitted or woven fabrics may be given after treatments with methylolating polymers for improved crease resistance.

The acrylic polymers can be grafted before spinning the fibre or after the fibre is formed. If grafting is carried out before spinning, the polymer will have modified solubility properties as well as physical properties which are different from a grafted spun fibre.

Dyeability of Acrylic Fibre

There has been a joint effort by the dyestuff manufacturer, the fibre producer , and the dyer to finisher to develop the variety of colours with good fastness and brilliance of shade available in acrylic fibres today.
The fibre producer has contributed to this success by modification of the basic polymer. This improvement is brought about by the incorporation or creation of acidic groups in the polymer and use of cationic or basic dyestuffs. The acidic group frequently used is the sulfonic acid or its salt which is carried into the polymer chain as a substituent of a vinyl benzene, allyloxy benzene, or diamino-stilbene monomer. Also, while the fibre is in the gel state, it can be treated with a sulfonic acid derivative and upon drying and scouring it will retain sufficient acid groups for cationic dyeability.

Picture 15

If the third monomer is a vinylpyridine or methylvinylpyridine, or contains a tertiary or quarteruary nitrogen in the molecule, substantivity to acid dyes may result.

Picture 16

A polar, nonionizable monomer containing functional groups, such as an alkohol or ketone, effords sites for complexing with certain dyes. Dyeability with dispersed dyes is also improved by almost any comonomer which alters the structure and reduces the density or compactness of the fibre structure.

CHEMICAL MODIFICATION OF POLYETHYLENE TEREPHTHALATE

The modification of polyethylene terephthalate may be acccmplished by the incorporation of small amounts of comonomers into the linear polyester. This may change the fibre's physical and chemical properties as well as necessitate new melt spinning conditions. In this section some of the more important property modifications will be discussed, regardless of whether the chemistry occurs before the formation of the fibre, i.e., in the polycondensation process, to the resin, or in aftertreatment of the basic fibre.

Dyeability

Due to the crystallinity of PETfibres and the hydrophobicity of the polymer, dyeing is difficult to accomplish. Disperse dyes with the aid of a "carrier" are used to obtain the variety on depth of colours that today's market requires. Dyeability can be imparted by incorporating a suitable comonomer which will change the character of the fibre's noncrystalline areas.

Modification of poly(ethylene terephthalate) by a dibasic acid resulted in adverse effects on mechanical, physical, and chemical properties. In fact, the quantity of a third component that can be tolerated without an unacceptable decrease in melting point or increased fibre shrinkage is small.

A review of the literature on copolyesters will show that hundreds of copolyesters have been prepared. The comonomers included alkyl diols and dicarboxylic acids, substituted acryl and alkylacryl diols, and dicarboxylic acids as well as a variety of difunctional heterocyclic compounds.

Picture 17

Picture 18

Cationic Dyeability (Basic)

To impart this dyeing property to polyester fibres, comonomers containing salts of sulfonic, sulfenic, and phosphonic and phosphinic acids appear acceptable.

Picture 19

The sodium salt of 5-sulfo-isophthalic acid a the 2,5-mole % level gives sufficient ionic dye sites for a commercial fibre with good cationic dyeability.

3,5-Dicarboxylphenylphosphonic acid or its salt is an example of a difunctional phosphorous compound that is claimed for basic dyeability.

Picture 20

Picture 21

Polyesters with an affinity for acid dyes, can be prepared by the use of comonomers containing nitrogen. Tertiary amine compounds containing either alkyl, aryl, aralkyl, or cycloalkyl groups have been claimed.

Picture 22

Picture 23

Difunctional triazoles such as 1-(carbethoxy-methyl)-4-(hydroxymethyl) -1,2,3-triazole may be useful in this area.

An other route for a modification is the cospinning of dye-acceptable polymers with polyester shown in

Picture 24

Grafting reactions on fibres can bring about a variety of chemical property changes, depending on the monomers used for grafting. Theoretically, the types of dyeability discussed earlier in the section can be achieved by grafting:

N-vinyllactams
vinyl-benzensulfonic acids
p-vinylbenzylamines, and
vinylphenylpolyglycol ethers

are a few of the monomer types which can control the type and extent of dye acceptance in polyester fibres.

CHEMICAL MODIFICATION OF POLYOLEFINS

The chemical modification of olefin fibres is economically prohibitive at present, but much research has been conducted in this area which will probably be utilized eventually. A number of problems have appeared which are germane to the development of chemically modified polyolefins.

Considerable degradation occurs in crosslinking polyolefins with high-energy radiation techniques although this modification process is possible under vacuum conditions with uv light. The reaction is accelerated by the presence of inorganic substances (TiO_2, Al_2O_3), but unfortunately, it is still slow, requiring 10-60h.

In general, the use of radiation is not a satisfactory method for modifying polyolefin fibre properties through the introduction of crosslinks. A second method for property modification is graft polymerisation. There are several ways to produce reactive sites in polyolefins, particularly in polypropylene.

One way is with a high-energy source such as γ-rays from a cobalt source, or even uv light can be used to produce free radicals. Chemically, an oxidizer such as tertiarybenzoyl peroxide or an O_2/O_3 gaseous mixture is adequate. The monomers which have been used in grafting reactions include:

Acrylonitrile
Styrene
Divinylbenzene
Vinylchloride
Vinylacetate
Vinylidene chloride

Vinyl sulfonic acids and salts
Acrylic acid
Acrylates
Methyacrylates
Vinylpyridines
Vinylpyrrolidinones

Some of these grafts improve physical properties such as strength, elongation, and heat resistance; others improve adhesive properties and wettability and the nitrogen-containing monomers and sulfonic acids improve dyeability with acid and basic dyes respectively.

The methods available for the synthesis of graft copolymers with polypropylen as the backbone are the radiation techniques used in several ways:

1) to form an active site on a preformed macromolecule in the presence of a polymerizable monomer;
2) to form a peroxidized polymer in the presence of oxygen which can then be used for a subsequent reaction for initiating the polymerization of a monomer;
3) preirradiation in vacuum to form trapped free radicals whose lifetime is prolongend at lower temperatures
4) radiation of an intimate mixture of two polymers producing two polymeric free radicals leading to a graft or interlinking of two different polymers.

In grafting reactions, however, there is a possibility of chain-transfer reactions occuring which results in the production of some homopolymer. These reactions can be characterized by a chain-transfer constant.
This constant represents the ratio of the velocity constant for transfer of chains to their growth constant.

Other examples of grafting are diazotization and degradation which produce free radicals by thermal and mechanical techniques.

The influence of structure is important in grafting. The initial rate is affected by the amorphous areas, their size and orientation, as well as segment mobility of the chains at various temperatures.

Chain-transfer reactions are another very common method for synthesizing graft copolymers. By its very nature the graft formed is in admixture with some homopolymer.
The difference between a chain-transfer raction, a polymeric radical transfer reaction, and a polymeric radical imitiated graft has not always made clear in the literature.
Hydroperoxid formation is a third method of producing grafted polyolefins. These may be formed at temperatures of 70-80° C with air, oxygen, or peroxy chemicals.

Cospinning of polymers is of growing importance in the fibre industry if the patent literature is any indicator. The properties of polypropylen fibres can be modified in this manner to give crimp, dyeability, and oxidative and thermal stability. On the other hand, the cospinning approach to modification frequently leads to difficulties, since the second polymeric component may act simply as a diluent and a plasticizer.

In cospinning polypropylen with polyethylene, the polyethylene seems to act as a plastizer and the best compatibility appears to be 75% polyethylene - 25% polypropylen. Other reports of this polymeric blend, while not agreeing on the most desirable polymer contents, show that the fibres contain continuous polypropylene and polyethylene fibrils. The resulting fibres

usually show abnormel behavior in their mechanical properties. Crimped polypropylene fibres can be produced by cospinning two different types of molten polypropylen. The polypropylen should vary in molecular weight distribution but they also should have a similar melt viscosity. Fibres containing such polymers can be produced from spinnerets as a side-by-side composite filament or as a sheat core composite.

Many other polymers are cospun with polypropylene for the principal objective of improving and modifying dyeabiltiy. The polymers vary from such common ones as polystyrene and polyacrylates to particular dye acceptor types such as polyamides, polyimines, polytriazoles, and polypyrrolidones.

The cospinning approach to polypropylene fibre modification is at present most useful for producing crimped or crimpable fibres and for improved dyeabilty.

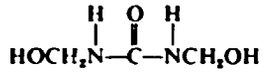
Frequently the properties are achieved at the expense of a decrease in another desirable physical property. Regardless, cospinning is an area where future progress may be anticipated for many melt-spun fibres.

I hope, that I could give you a short summary of the large area of chemical fibre modifications with my report. I could not speak so exactly about many important things, becouse the research of fibre modifications has expanded very much in the last years and also the number of publications increased more and more.

Picture 1

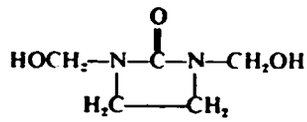
(1) Methylolureas

example:



(2) Cyclic alkyleneureas(*13*)

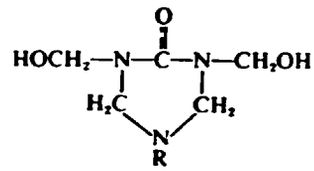
example:



1,3-bis(hydroxymethyl)-2-imidazolidinone (DMEU)

(3) Triazone

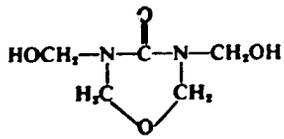
example:



Picture 2

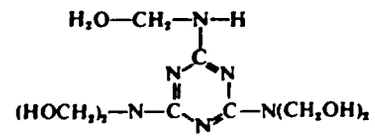
(4) Uron

example:



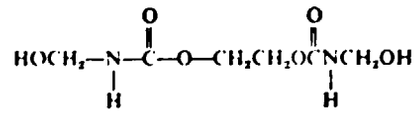
(5) Triazines

example:



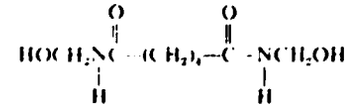
(6) Carbamates

example:



(7) Methylolamides

example:



Picture 3

Finishing Process	State of Cellulosic Fibre Reaction	Constitution of Basic Crosslinking Agent
Dry crosslinking (elevated temp.) Conventional finish Flash curing Permanent Press Combined finishing and dyeing	De-swollen Acid catalysis	X · HN · CO · NH · X X · H₂NCO · (CH₂)ₙ · CONH · X X · HNC(O)O(CH₂)ₙO(O)CNH · X X · O(CH₂)ₙO · X ROCONX₂ ACONX₂
Moist crosslinking (various temps.) Moist-batch W 111 Speed-dry	Partially swollen Special acid catalysts	Special types of
Wet crosslinking (low temps.) Alkaline (a) Acid (b)	Swollen Alkaline or acid catalysis	S (CH₂ · CH₂ · OSO₃)₂2Na (a) CH₂ CH CH₂Cl (a)
Multi-stage crosslinking (various temps.) Bel-O-Fast Teb-X-Cel Ambivalent crosslinking	De-swollen and swollen Acid and alkaline catalysis	CH₂ CH · CH₂Cl ..... 1st Stage S (CH₂ · CH₂ · OSO₃)₂2Na ..... 2nd Stage CH₂ = CH – C(=O) – NH – X .....
Special finishes Oil-repellent (a) Water-repellent (b)	De-swollen Acid catalysis	C₇F₁₅ · CONR₁R₂ (a) C₇F₁₅ · SO₂NR₁R₂ (a)

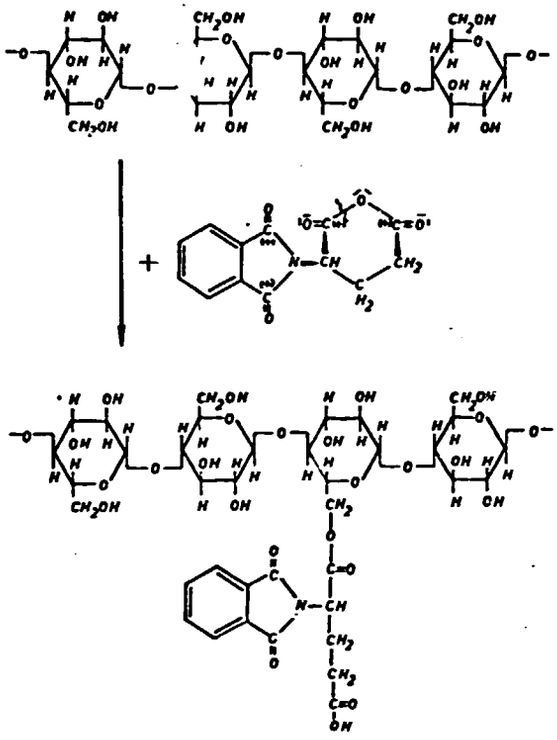
Table 1 Resin-finishing processes and the basic crosslinking agents used

Picture 4

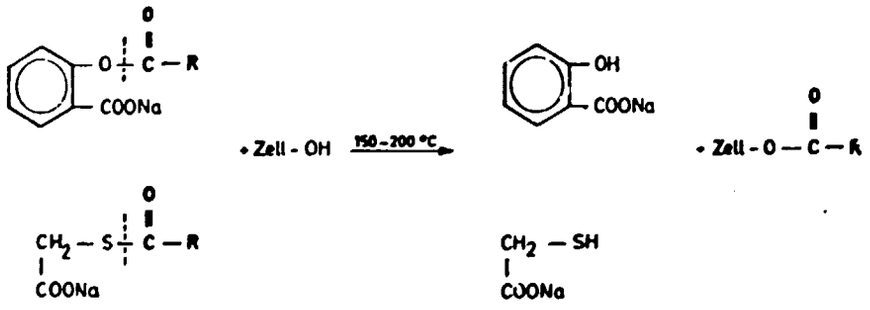
$$2\ Cell\text{-}OH + R(CH_2OH)_2 \longrightarrow$$

$$Cell\text{-}O\text{-}CH_2\text{-}R\text{-}CH_2\text{-}O\text{-}Cell + 2H_2O$$

Picture 5

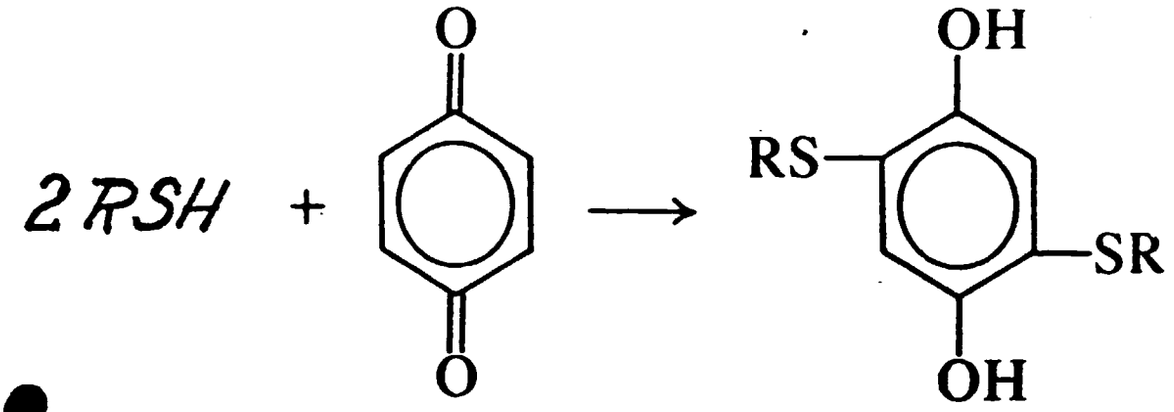


Picture 6

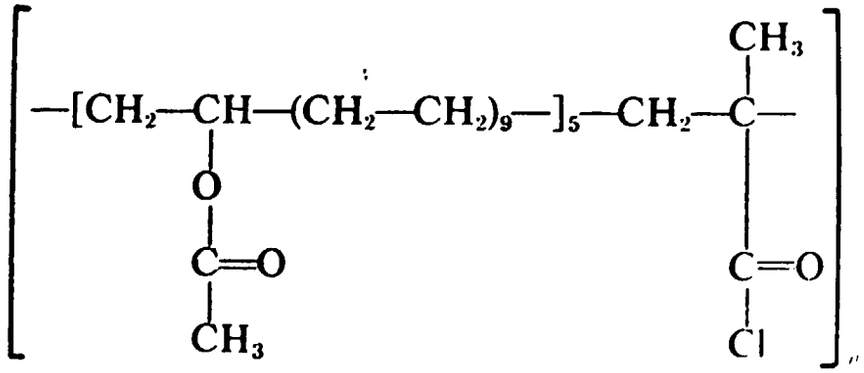


Reaktionsschema der Umesterung (1)

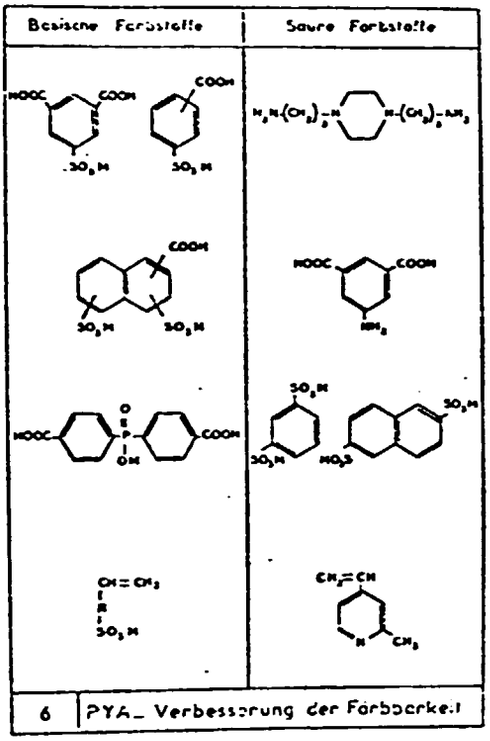
Picture 7



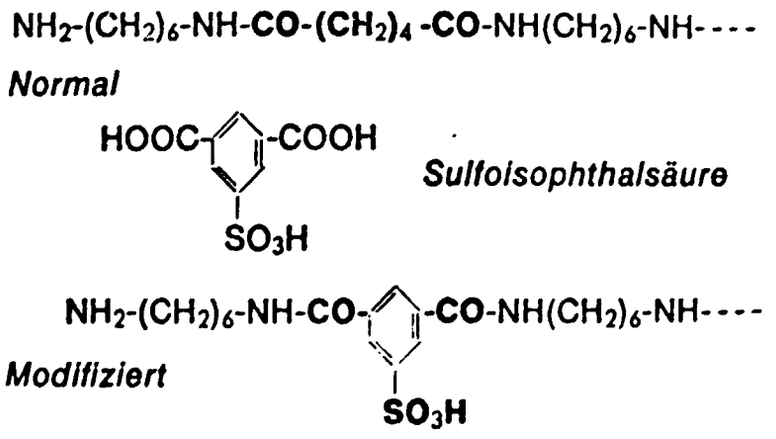
Picture 8



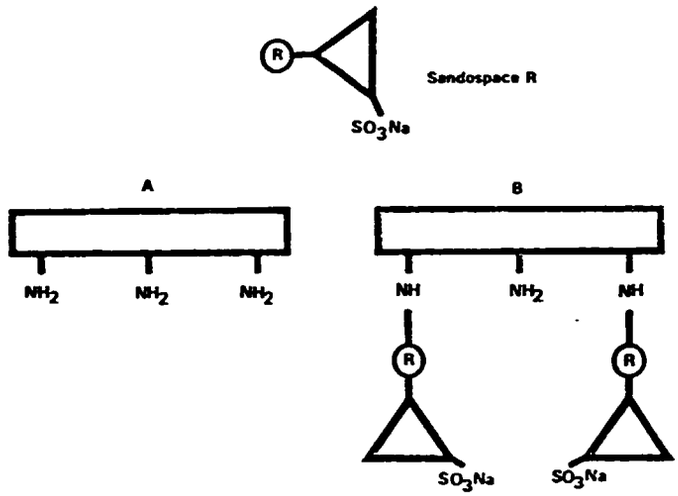
Picture 9



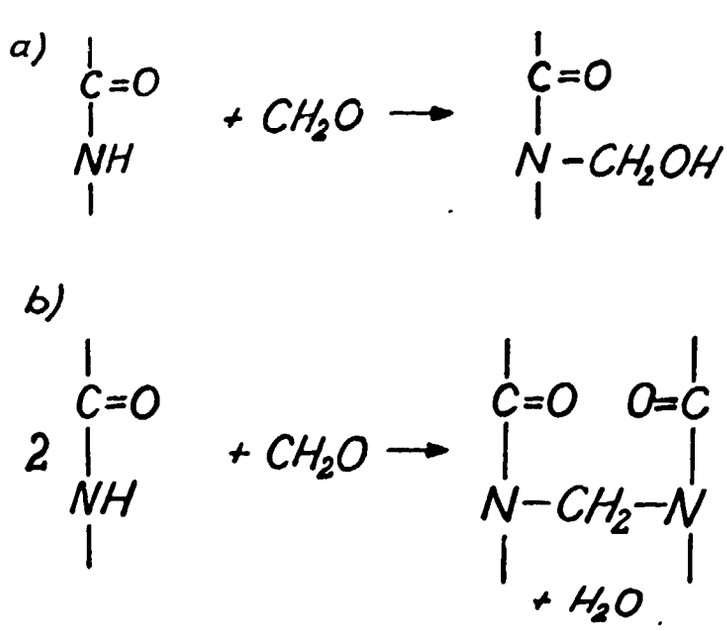
Picture 1o



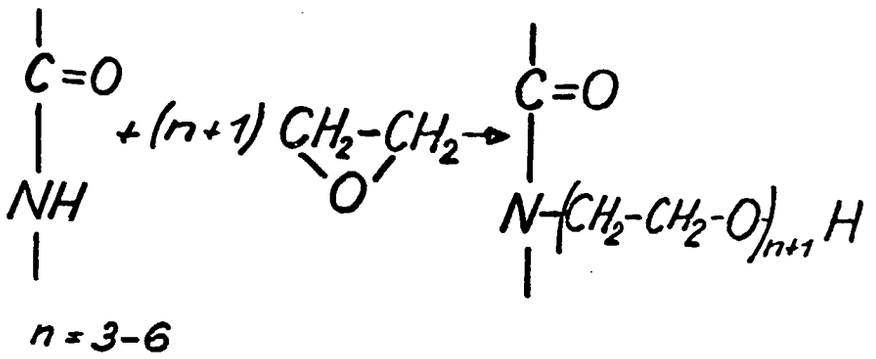
Picture 11



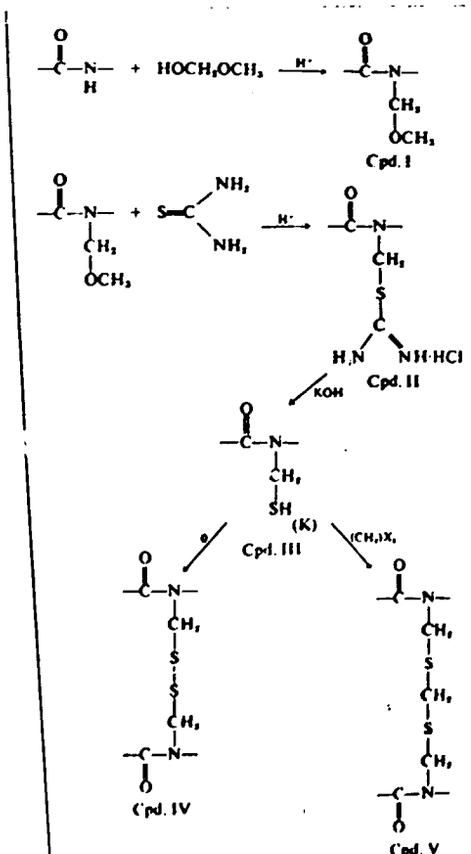
Picture 12



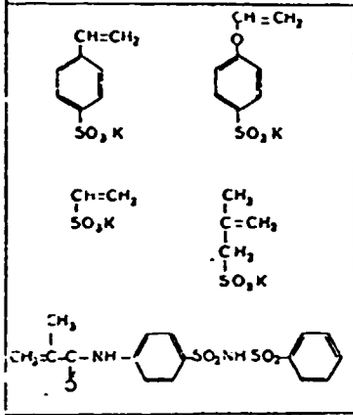
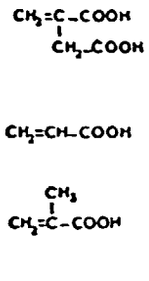
Picture 13



Picture 14

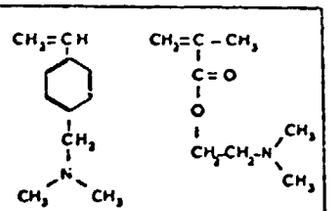
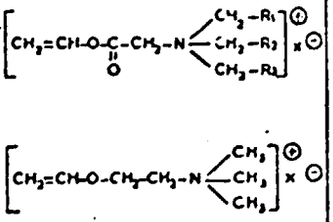
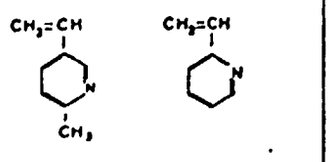


Picture 15

Sulfonsäure	Carbonsäure
	

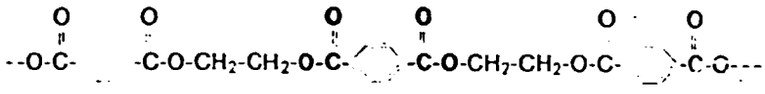
7 | PAN – Farbbarkeit mit basischen Farbstoffen

Picture 16

Amine	
Quartäres Ammonium	
Stickstoff-haltige Heterocyclen	

8 | PAN Färbbarkeit mit sauren Farbstoffen

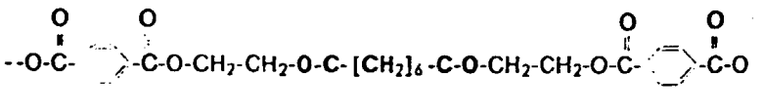
Picture 17



Normal

$$HOOC\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}COOH$$

Korksäure

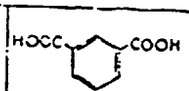
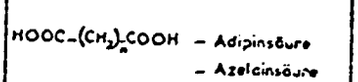
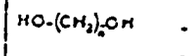
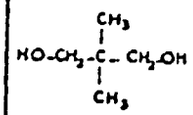
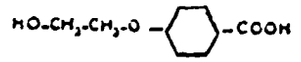
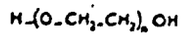
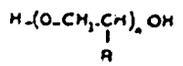


Modifiziert

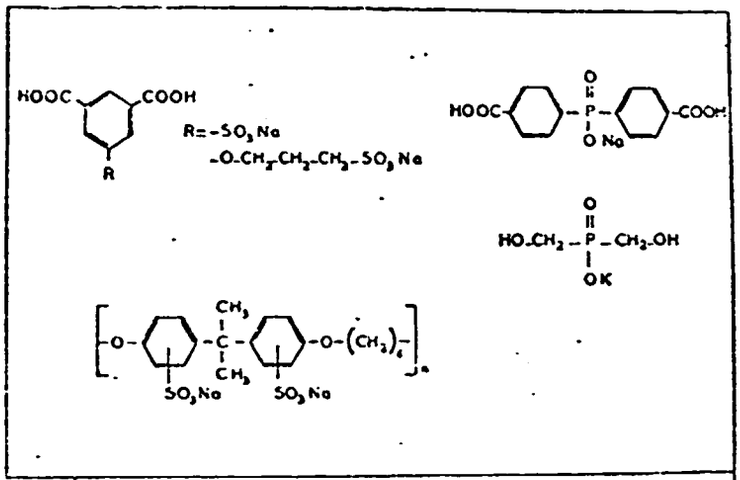
Bild 3 Deep dyeing Polyesterfaser durch Modifizierung mit aliphatischen Carbonsäuren

→

Picture 18

Comonomere Dicarbonsäuren	  – Adipinsäure – Azelainsäure – Sebazinsäure
Comonomere Diole	 – 1,4 Butandiol – 1,6 Hexandiol 
Verschiedene Polyalkylenoxid	  
2	PES. Farbbarkeit für Dispersionsfarbstoffe 100 °C

Picture 19



3	PES-Färbbarkeit mit basischen Farbstoffen

Picture 2o

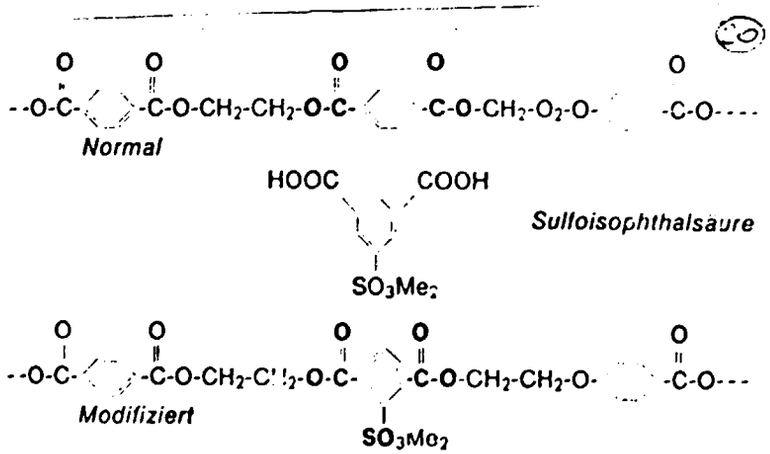


Bild 1 Mit kationischen Farbstoffen färbbare Polyester-Faser; S-Modifizierung

Picture 21

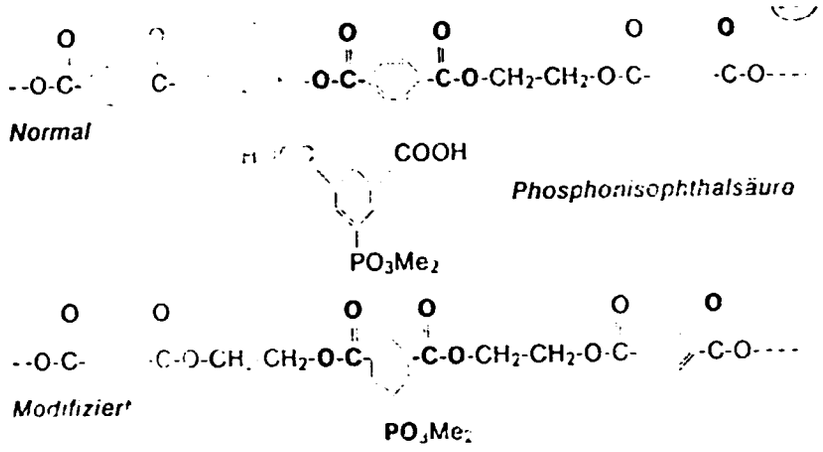
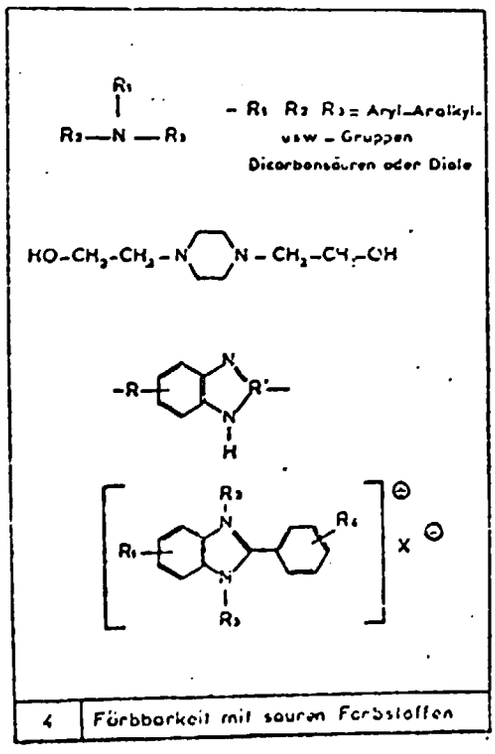
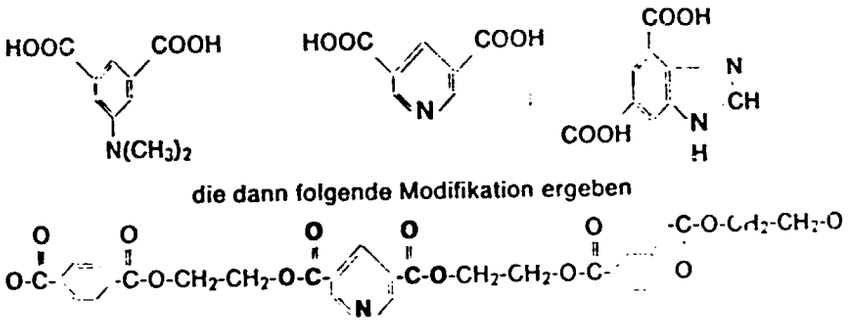


Bild 2 Mit kationischen Farbstoffen färbbare Polyesterfasern durch P-Modifizierung

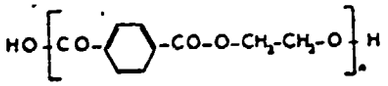
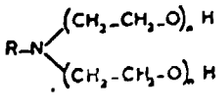
Picture 22



Picture 23



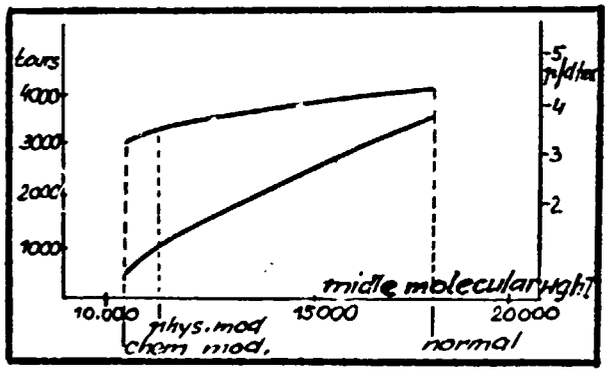
Picture 24

Polyester - modifizierte Polyamid-Mischung	
PES 50 – 99 % Modifiziertes PYA 1 – 50 %	 Copolymere 6 / 6 T 70 / 30 ⊕ Modifizierungsmittel 
5	Modifizierte Fc oberfl

Chemical modification of fibers
Polyethylentherephthalat-fiber

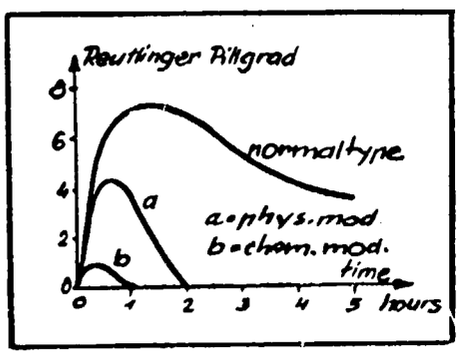
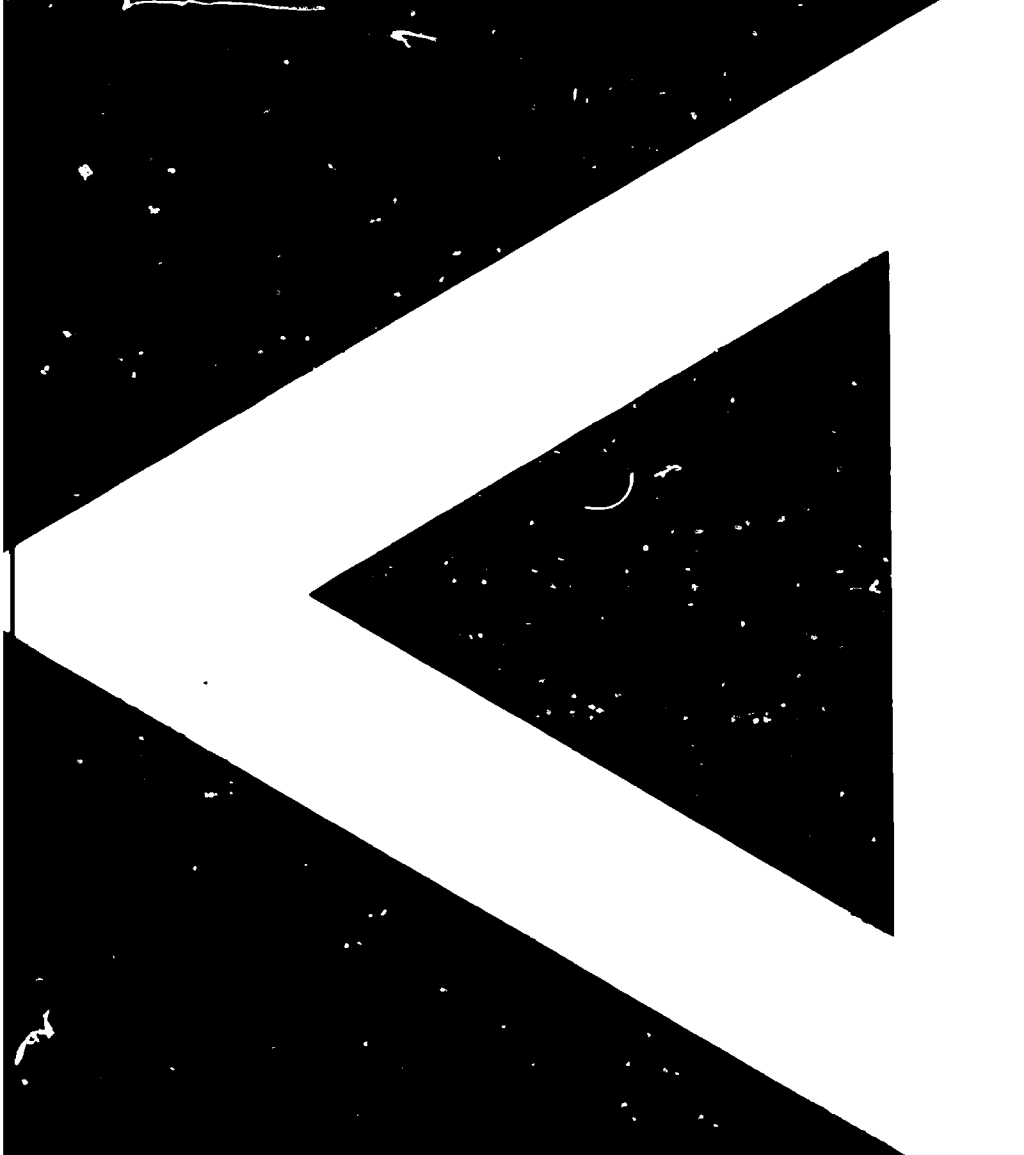
The Polyethylenterephthalat-fiber is the most important chemical fiber, since 1972 than polyamide. In the year of 1972 the world production of PE-fiber was 2,5 Mill.tons, the production in western europe 650.000 tons of spinnfibers and filaments.
On account of the variable using the PE-fiber is today the most important syntetic fiber for men and women clothing and dressing for children. Also she had a great market for home textiles and for technique textiles.
The greatest quantity is today the production of standard-types, e.q. the wool-like and cotton-like types, so as even an filamentyarn. The development of modified PE-fibers had given new properties and the modified fibers becames a good place in the production.

On of the first problems, in the begin of the PE-development in the year 1955 was the pilling problem. It-s well known, that pills are formed because of the high density and the high Flexlife of PE-fibers. The pills can not break so quickly as these of the wool.
Now the fiber production developed types of PE-fibers with a little lower density, but a strong lower Flexlife. This can be made by a control of the molecular weight - physical modification, but also in the next years to chemical modified types e.q. Trevira 350 and Dacron 65.



We can see, that because of the chemical modification the types Trevira 350 and Dacron 65 in the pilling effect go under the values only pysical modified fibers. The chemical modified fibers give a wool-like hand, soft and bull textile products.

In the next picture you can see pilling-curves, measured on the Random Tumble Pilling Tester and to estimate by the "Reutlinger Pillgrad"



The curves shown that the chemical modified types has only a little or no pilling effect!
The development in this part is finished and we can say, that the poor pilling type is today not a special fiber - it is a standard fiber.