July 11, 1961 TETSURO OSUGI ET AL 2,992,204

POLYVINYL ALCOHOL FILAMENTS OF IMPROVED DYE AFFINITY

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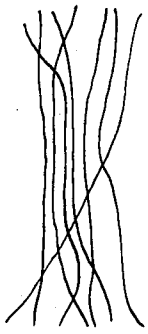


FIG. 1

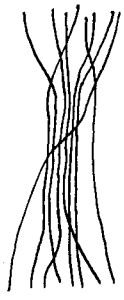


FIG. 2

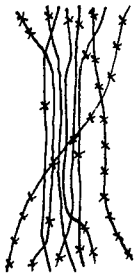


FIG. 3

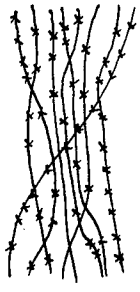


FIG. 4

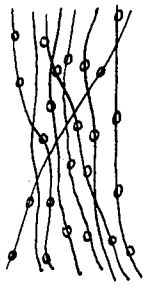


FIG. 5

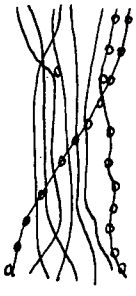


FIG. 6

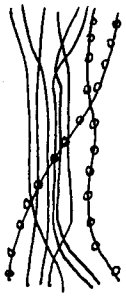


FIG. 7

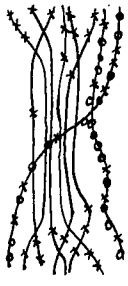


FIG. 8

——————— MOLECULE OF POLYVINYL ALCOHOL

—x— FORMALIZED GROUP

—o— AMINO-ACETALIZED GROUP

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2,992,204

POLYVINYL ALCOHOL FILAMENTS OF IMPROVED DYE AFFINITY

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7 Claims. (Cl. 260—45.5)

This invention relates to improved synthetic fibers of polyvinyl alcohol, more particularly to such fibers which have an increased affinity to direct acid and acid mordant dyestuffs and also resistance to boiling water, and to a process for preparing such fibers.

It has been known that fibers of hydroxylated polymers such as polyvinyl alcohol (PVA) or hydrolyzed copolymers of vinyl esters with minor amounts of polymerizable vinyl or vinylidene compounds may be obtained by dry or wet spinning from their aqueous solutions. But these fibers are characterized by an undesirable sensitivity to water, particularly to hot water; if dipped in water at ordinary temperature, they shrink by more than ten percent of their original length and they dissolve in water of 70–90° C.

In order to avoid such disadvantages, the freshly spun fibers are usually subjected to a heat-treatment at a temperature of 200° C. to 250° C. and then acetalized with formaldehyde. The wet softening temperature of heat-treated fibers, i.e. the temperature at which the fiber shrinks 10% of its original length, when dipped in water for 30 minutes, can be raised up to 60° C. to 100° C., but the fibers still dissolve when the temperature of the water is further raised by about 10 degrees. If after heat-treatment, the fiber is subjected to formalization, its wet-softening temperature is increased up to 100° C. to 130° C. and it is not dissolved even in hot water of 150° C.; it can, therefore, be considered that the wet-heat resistance of the fiber thus treated is sufficient for practical uses.

On the other hand, the heat-treated and formalized polyvinyl alcohol fibers have the disadvantage of poor dyeability. Since polyvinyl alcohol fibers do not contain basic nitrogen, they can not be dyed with most acid and acid mordant dyestuffs, and are only somewhat stained with some of these dyes. Untreated polyvinyl alcohol fibers may have almost the same dyeability as cellulose fibers due to the presence of hydroxyl groups, but after a heat-treatment the degree of crystallization of the polyvinyl alcohol molecules is increased and the accessible hydroxyl groups of said molecules decrease so that the affinity of said fibers to direct dyestuffs becomes almost the same or even a little lower than that of cotton fibers. Moreover, when the heat-treated polyvinyl alcohol fibers are acetalized by formaldehyde, the dyeability usually decreases further due to the fact that the accessible hydroxyl groups of polyvinyl alcohol molecules remaining after the heat-treatment are substantially blocked by formaldehyde. Thus the dye-absorption of the heat-treated and then formalized polyvinyl alcohol fibers with respect to direct dyestuffs is in general about 30 to 80% of that of cotton fibers.

When polyvinyl alcohol fibers are subjected to partial formalization in an aqueous solution directly after they were spun, without intermediate heat-treatment, the affinity to direct dyes is very good. This is due to the large increase of accessible hydroxyl groups by the swelling of the fibers during formalization; its effect overcomes the blocking of the accessible hydroxyl groups by the

formalization so that the total amount of accessible hydroxyl groups increases considerably compared with fibers heat-treated before formalization. However, the wet-softening temperature of such fibers is below 60° C., and the fibers shrink considerably in boiling water and become gelated and sticky. As the ratio of formalization increases, the affinity to direct dyestuffs decreases until the fibers can no longer by dyed but only stained, while the shrinkage in boiling water is not considerably improved.

On the other hand, it has been known that it is necessary to introduce basic nitrogen in order to impart affinity to acid colours and acid mordant colours. According to a method described in British patent specification No. 509,012, films and fibers can be obtained by acetalizing polyvinyl alcohol or polyvinyl acetate with amino-carbonyl compounds such as p-dimethyl or p-diethyl-aminobenzaldehyde, or p-aminoacetophenone. It may be expected that such fibers would have an improved affinity to acid and acid mordant dyes, but it is impossible to impart to the fibers a dry and wet heat resistance sufficient for practical applications. It is impossible to raise the wet heat resistance over 60° C. by subjecting said fibers to a heat-treatment. Also, such fibers when acetalized with formaldehyde after a heat-treatment, were not yet resistant to boiling water. Their softening point in air (the air temperature at which the fibers shrink 10% after a treatment of 5 minutes) could not be exactly determined since it is affected by the degree of amino-acetalization, but it is usually below 150° C. Even if the amino-acetalized polyvinyl alcohol in which the amino-acetal groups are distributed at random for each molecule of polyvinyl alcohol is spun alone into a fiber and then heat-treated, the formation of definite crystallites between polyvinyl alcohol molecules can not be expected since the amino-acetal group has a large molecular volume and hinders crystallization of polyvinyl alcohol molecules; when it is further acetalized a comparatively homogeneous acetalization can be effected throughout each fiber so that a desirable improvement of the dry and wet heat resistance can not be obtained.

It is a principal object of the invention to provide polyvinyl alcohol fibers which combine good resistance to boiling water with improved dyeing properties.

It is another object of the invention to provide a method for producing such fibers.

Other objects and advantages will be apparent from a consideration of the specification and claims.

The new product according to this invention is a fiber consisting essentially of oriented polyvinyl alcohol-polyvinyl nonamino-acetal and polyvinyl alcohol-polyvinyl nonamino-acetal-polyvinyl amino-acetal, in which the former is contained to the extent of at least 30% by weight, and in which between 0.2 and 10% of the total hydroxyl groups are acetalized by an amino-aldehyde and between 5 and 60% of the total hydroxyl groups are acetalized by a nonamino-aldehyde. The novel fiber and its preparation will be described more in detail with reference to the accompanying drawings, which illustrate diagrammatically the arrangement of the molecular chains of various fibers, based on their physical and chemical properties and X-ray patterns. In the drawings,

FIG. 1 shows diagrammatically the moderately oriented molecular arrangement of a polyvinyl alcohol fiber which is not heat-treated after spinning;

FIG. 2 is a similar view for a heat-treated polyvinyl alcohol fiber;

FIG. 3 is a similar view of a polyvinyl alcohol fiber which has been formalized after heat-treatment;

FIG. 4 is the same view of a polyvinyl alcohol fiber formalized without heat-treatment after spinning;

FIG. 5 shows diagrammatically the chain arrangements

of a filament spun from polyvinyl aminoacetal alone;

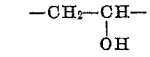
FIG. 6 shows diagrammatically the arrangements of molecular chains of a filament spun from a spinning solution containing polyvinyl aminoacetal and polyvinyl alcohol according to this invention;

FIG. 7 shows the same diagram after the above mentioned filament has been heat-treated, and

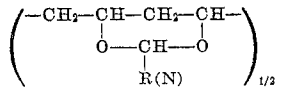
FIG. 8 shows the same view of the filament mentioned in FIG. 6 after heat-treatment and formalization.

The X-ray pattern does not show a substantial difference between polyvinyl alcohol fibers obtained without (FIG. 1) or with a subsequent heat-treatment (FIG. 2), though the diagram of the latter is somewhat sharper. The X-ray pattern of the formalized fiber after heat-treatment (FIG. 3) shows absolutely no change so that it is evident that the formalization is effected on the amorphous portion of the molecular arrangement. By formalization after spinning without heat-treatment (FIG. 4), the X-ray pattern of the fiber becomes gradually indefinite to show the decrease of crystallites.

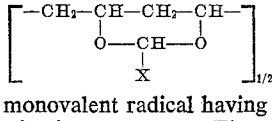
In order to obtain fibers according to this invention, polyvinyl alcohol (the term "polyvinyl alcohol" is used to define a synthetic linear polymer having hydroxyl groups directly attached to the carbon atoms of the polymer chain, said polymer consisting to the extent of at least 95% by weight, of vinyl alcohol, $-CH_2CHOH-$, units) and polyvinyl amino-acetal which consists of vinyl alcohol



units and amino-acetalized vinyl alcohol



units, wherein R(N) is a monovalent radical having 1–3 basic nitrogen atoms and carbon atoms of up to 20, are mixed to form a polymer blend, said polymer blend consisting to the extent of at least 30% by weight, of polyvinyl alcohol, and the ratio of amino-acetalized vinyl alcohol units to total vinyl alcohol units being between 1:499 and 1:9; the aqueous solution of said blend is spun to filaments, and the filaments are stretched to the draw ratio of 2/1–12/1; the stretched and oriented filaments are then subjected to a heat-treatment until they have a water softening temperature of more than 60° C., and finally the heat-set oriented filaments are treated with a nonamino-monoaldehyde having up to 20 carbon atoms until 5–60% of the hydroxyl groups of the filaments are acetalized. The acetalized vinyl alcohol units have the formula

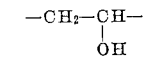


wherein X is a monovalent radical having 1 to 19 carbon atoms and no basic nitrogen atoms. The ratio of the total nonamino-acetalized vinyl alcohol units to the sum of the total of the vinyl alcohol units and the amino-acetalized vinyl alcohol units in the resulting filaments is in the range 1:19 to 1:0.67.

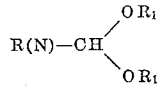
If a fiber consisting of polyvinyl amino-acetal alone is spun, even though the degree of amino-acetalization is very low such as 0.5 mol percent (the degree of acetalization is shown by percent of acetalized hydroxyl groups to the initial total hydroxyl groups) the amino-acetal groups which are comparatively homogeneously distributed over all the polymer chains as above described will disturb the intermolecular crystallization of polyvinyl alcohol at the succeeding heat-treatment so that it is impossible to assure higher dry and wet heat resistance by acetalization with nonamino-aldehyde in the next step. On the other hand, if polyvinyl amino-acetal is blended with polyvinyl alcohol at such a ratio that the latter is

at least 30% by weight and the average degree of amino-acetalization of the blend is 0.2 mol percent to 10 mol percent, and the aqueous solution of such polymer blend is spun to filaments, the polyvinyl alcohol molecules in said filaments crystallize in the succeeding heat-treatment process to such an extent that the wet softening temperature after the heat-treatment can easily be raised above 60° C., and if it is further nonamino-acetalized, a small part of polyvinyl alcohol molecules which remain uncrystallized, and the major part of polyvinyl amino-acetalized molecules which are considered to be at amorphous portions, can be acetalized, thereby raising the softening temperatures in air to more than 180° C. and the wet softening temperature to more than 100° C. These chain molecular arrangements are shown in FIGS. 6–8, wherein FIG. 6 illustrates those after spinning, FIG. 7 those after spinning and heat-treatment, and FIG. 8 those after spinning, heat-treatment and acetalization.

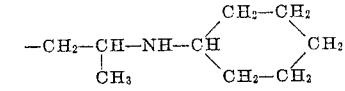
As polyvinyl alcohol, macromolecular, synthetic, linear hydroxylated polymers may be used in which at least 95% of the weight consists of vinyl alcohol units



Polyvinyl amino-acetal can be obtained by reacting polyvinyl alcohol or polyvinyl esters of organic acids, in the presence of catalysts, with various amino-aldehydes, R(N)—CHO, or their acetals



with lower alcohols, wherein R_1 represents a methyl or ethyl group. It is convenient to add to the solution of the reactants an inorganic acid such as sulphuric acid, hydrochloric acid, phosphoric acid or the like as catalyst. As an example of suitable reacting conditions an aqueous solution containing 6% of polyvinyl alcohol, 6.2% of sulphuric acid, and 5% of beta-cyclohexylamino-butyraldehyde-dimethylacetal for which R(N)— is



is treated at the temperature of 70° C. for 10 hours. The obtained reaction product has a degree of acetalization of 31.7 mol percent. The conversion of initially added amino-acetal is 93.3%. This product is dialysed to remove sulphuric acid and unreacted amino-acetal, and the polyvinyl alcohol is added to the solution and dissolved therein by heating, whereupon the resulting solution can be used as spinning solution. Alternatively, the above reaction solution need not be dialyzed but a dilute aqueous solution of sodium hydroxide is slowly added to neutralize sulphuric acid; subsequently, an aqueous solution of polyvinyl alcohol is added, and after concentration the whole mixture can be used as spinning solution. In another modification, the solution of the recited polymers is dialyzed and concentrated by evaporating the water, whereby solid polyvinyl amino-acetal is obtained in the form of a film or chips, which are dissolved in water together with polyvinyl alcohol to prepare the spinning solution. As the polyvinyl amino-acetals are found mainly in the amorphous parts of the spun filaments, the polymer blend may contain, besides vinyl alcohol and amino-acetalized vinyl alcohol groups, other various polymerizable ethylenic groups, such as ethylene, vinyl acetate, methyl-methacrylate, or methacrylamide; also formalized butyraldehyde, or acetalized or oxyacetalized vinyl alcohol groups within the limits in which the water solubility of the polyvinyl amino-acetal and their compatibility with the aqueous solution of polyvinyl alcohol is maintained.

The first step of this invention consists in spinning an aqueous solution of a polymer blend of polyvinyl al-

cohol and polyvinyl amino-acetal, and it is essential that the polymer blend should contain at least 30% by weight of polyvinyl alcohol. This condition is particularly important when the average degree of amino-acetalization in the blend is comparatively high, since the higher the average degree of amino-acetalization, the more difficult is it to ensure the hot water resistance. Though it is easy to attain a satisfactory hot water resistance with a blend having an average degree of amino-acetalization of less than 0.2 mol percent, the improvement in dyeability is insufficient at such a low amino-acetalization degree. On the other hand, with a blend having an average degree of amino-acetalization higher than 10 mol percent, it becomes difficult to obtain a satisfactory resistance to boiling water after the heat-treatment and nonamino-acetalization. This is especially the case when the weight percent of polyvinyl alcohol in the blend is low. As the average degree of amino-acetalization of the blend increases, the dyeability is improved, and a satisfactory dyeability can be obtained at about 2–3 mol percent. If the average degree of amino-acetalization remains the same, the dyeing properties of the filaments seem to improve with decreasing proportions of polyvinyl alcohol in the blend. On the other hand, as may be concluded from FIGS. 1 to 8, the required hot water resistance can be more easily ensured as the content of polyvinyl alcohol in the blend is increased. The degree of amino-acetalization of polyvinyl amino-acetal can be adjusted as desired as long as the above mentioned conditions, i.e. a content of polyvinyl alcohol in the blend of more than 30 weight percent and an average degree of amino-acetalization of the blend of 0.2 to 10 mol percent, is satisfied.

Spinning of the polymer blend into filaments is accomplished by any of the known dry or wet spinning methods. Dry spinning may be carried out by extruding an aqueous solution of the polymer blend, e.g., a solution of 25–60% concentration of the polymer blend, into a chamber at a temperature of 40–180° C. In wet spinning, an aqueous solution of polymer blend of 10–30% is extruded into an aqueous salt bath maintained at a temperature of 25° C. to 60° C. As suitable baths, we may mention a concentrated solution of sodium sulphate, potassium sulphate, ammonium sulphate, sodium dihydrogen phosphate, and the like.

Wet-spinning of the polymer blend can be carried out under conditions similar to that of polyvinyl alcohol alone, though the coagulating velocity is somewhat lower. To increase the coagulating velocity, it is of advantage to add about 5 to 20% based on the weight of polymer, of the above mentioned inorganic coagulating salts. Thereby also the cross-sectional shape of the filament is improved to a nearly round shape from a kidney shape.

The wet-spinning of a polymer blend according to this invention has the advantage that the obtained filaments exhibit a more homogeneous sectional structure than obtainable by wet-spinning of polyvinyl alcohol alone. The latter fiber has a sectional structure where a porous core portion is located inside a transparent thin skin layer. In contradistinction thereto, the filament obtained by wet-spinning of the polymer blend according to this invention has only a very indistinctive slight porous core or almost no core at all, and seems entirely transparent. This structure results in an improved color brilliancy and color concentration for the same dye absorption.

As the second step of this invention, the spun filaments are stretched, whereby the orientation of the polymer molecules is improved and the tensile strength is increased. In dry spinning, the filaments can be stretched to a draw ratio of 2/1 to 4/1 by cold drawing under the normal atmosphere. In wet spinning, the filaments can be stretched up to the strength of 4 g./d. by means of guide stretch or roller stretch. In order to obtain filaments having a strength higher than about 4 g./d., the filaments are usually stretched further in a salt bath of a concentration of about 5% to saturation, at a temperature of 40–98° C., or in air, nitrogen, carbon dioxide or other inert gases or any substantially anhydrous fluid medium which is inert, that is which does not dissolve or injure the filaments, such as oil, molten metals or alloys or the like, at temperatures of 70° C. to 250° C., which must be at least 2° C. below the temperature at which the filaments become sticky. The total stretch can be carried out up to the draw ratio of 2/1. It is possible to obtain by this stretching filaments having a maximum strength of 10 to 12 g./d.

The third step of this invention consists in heat-setting the oriented filaments, whereby the arrangement of the polymer chains is improved so as to form more definite crystallites with each other; in this way, the wet softening temperature of the filaments is raised above 60° C. and the swelling and shrinkage which deteriorate the nature of fiber in the succeeding acetalization step, are substantially avoided. The heat-treatment is carried out, without positively stretching the filaments, in air, nitrogen, carbon dioxide or other inert gases, or in any substantially anhydrous fluid medium which is inert, that is which does not dissolve or injure the filaments, such as oil, molten metals or alloys or the like, at a temperature of 200–260° C. and at least 2° C. below the temperature at which the filaments become sticky, for 0.2 second to 30 minutes; the heat treatment may also be effected in water vapor alone or mixed, with air, whereby the water vapor may have a vapor pressure up to 10 kgs./cm.^{2} above atmospheric pressure, at a temperature of 140 to 230° C. and at least 2° C. below the temperature at which the filaments become sticky for 1 second to 1 hour until the wet softening temperature of the filaments is higher than 60° C. If the treatment is applied to freely suspended filaments, crimped fibers may be obtained.

The filaments of the polymer blend of this invention are liable to be more easily yellowed by heat in the stretching, more particularly in the heat-treatment step than filaments spun from polyvinyl alcohol. The yellowing due to heat is particularly noticeable when the filaments are heat-treated in the presence of air. If compared under the same stretching conditions, less yellowing takes place when the filaments are heat-treated at higher temperatures for a shorter period of time than at lower temperatures for a longer period of time. Therefore, it is preferable to treat filaments of small total denier at higher temperatures within a shorter period of time. For example, if filaments of about 200 drs. are treated at 240° C. for 3 seconds, a uniform heat-treatment can be effected, and pure white filaments having a wet softening temperature of 95° C. are obtained. On the other hand, at 5000 drs. it is necessary to carry out the treatment at 235° C. for 30 seconds in order to effect a uniform heat-treatment, and slightly yellow colored filaments are obtained having a wet softening temperature of 93° C. 50,000 drs. yarn requires a treatment at 230° C. for 2 minutes, which produces light yellow filaments having a wet softening temperature of 91° C. At 220° C., the same yarn requires 5 minutes in order to obtain filaments having a wet softening temperature of 91° C., and it is colored yellow. In order to minimize the coloring, we may add sodium hypophosphite of about 0.5 to 3% to the spinning solution, or 5 g./l. to 40 g./l. to the coagulating bath or to the second bath for stretching. In order to avoid as far as possible contact with air to prevent the coloring, the heating is preferably carried out in nitrogen, carbon dioxide, molten metal or water vapour. However, the yellow discoloration can be substantially removed by bleaching with hydrogen peroxide, sodium hypochlorite, or sodium chlorite, and pure white filaments can be ob-

tained by a further treatment with fluorescent bleaching agents.

The last step consists in treating the oriented, heat-set filaments with various insolubilizing agents to make the filaments insoluble in water. The heat-set filament, even though heat-treated under any conditions, completely dissolves in hot water of 70 to 110° C., or is at least converted to a gel and loses the filament structure. By processing such a filament with insolubilizing agents, a filament is obtained, which actually does not dissolve in hot water of 150° C. and which does not show more than 10% shrinkage after treated in hot water of a temperature of 100° C. to 130° C. for 30 minutes. Preferred insolubilizing agents are nonamino-mono-aldehydes having up to 20 carbon atoms, such as formaldehyde, acetaldehyde, propionaldehyde, butyraldehydes, valeraldehydes, hexaldehydes, heptaldehydes, octylaldehydes, nonylaldehydes, laurylaldehydes, acrolein, crotonaldehyde, chloroacetaldehyde, bromoacetaldehyde, benzaldehyde, chlorobenzaldehydes, nitrobenzaldehydes, hexahydrobenzaldehyde, furfural and naphthaldehyde. Moreover, inorganic insolubilizing agents such as titanyl sulphate, potassium bichromate, sodium bichromate and ammonium bichromate may be used. For the acetalization with aldehydes, preferably catalysts such as sulphuric acid, hydrochloric acid and phosphoric acid are used. As reaction medium, an aqueous solution is most suitable. The treatment is carried out usually in an aqueous solution having a catalyst concentration of 0.2–25% and an aldehyde concentration of 0.2–10% and containing 0–25% of a salt having coagulating properties such as sodium, potassium or ammonium sulphate, sodium or potassium chloride, or sodium nitrate, at a temperature of 40–95° C. until 5 to 60% of the hydroxyl groups in the filament have reacted with the aldehyde. Some aldehydes which are insoluble or difficultly soluble in water can be emulsified, dispersed or solubilized in the aqueous medium by adding 0.05 to 5% of surface active agents, and the reaction can be carried out without addition of organic solvents. Filaments acetalized with higher aldehydes having more than 4 carbon atoms have improved elastic recovery compared with filaments acetalized with a lower aldehyde. Generally, a filament spun from polyvinyl alcohol alone, and heat-treated and acetalized with higher aldehydes has almost perfect dye-resistance. It is therefore surprising that filaments spun from a blend of polyvinyl alcohol and polyvinyl amino-acetal according to this invention, when heat-treated and acetalized with higher aldehydes, exhibit almost perfect dye-exhaustion under ordinary dyeing conditions, though the dye-exhaustion is slightly lower than that of corresponding filaments acetalized with lower aldehydes. Our method provides synthetic fibers on polyvinyl alcohol basis of excellent resilience and at the same time improved affinity to dyestuffs.

The invention is illustrated in greater detail by the following examples, in which parts are by weight unless otherwise stated, and the degree of acetalization is shown as the percentage of acetalized hydroxyl groups calculated on the total amount of initial hydroxyl groups.

Example 1

65 parts of monomeric vinyl acetate containing 0.05% of benzoyl peroxide were heated at 70° C. for about 4 hours until about 50% of the vinyl acetate was polymerized, then a solution of 0.2 part of benzoyl peroxide and 35 parts of methanol was added thereto and the mixture was further heated at 60° C. for 30 hours to complete the polymerization.

The obtained polyvinyl acetate was dissolved in methanol to a 20% solution and hydrolyzed with a conc. aqueous sodium hydroxide solution. The resulting polyvinyl alcohol had a polymerization degree of 1600 and contained still 0.2 mol percent of vinyl acetate.

Aqueous solutions containing 6% of said polyvinyl alcohol and 5% of sulfuric acid were amino-acetalized at 80° C. for 15 minutes with beta-aminobutyraldehyde in the following concentrations:

(1) 0.08% (2) 0.12% (3) 0.12% (4) 0.3% (5) 0.5%

Subsequently, the reaction products were dialyzed, and the water was evaporated by pouring the mixture on a flat plate. The degree of amino-acetalization of the resulting films of polyvinyl amino-acetal was respectively

(1) 0.5% (2) 1.2% (3) 2.2% (4) 3.8% (5) 5.2%

Aqueous solutions of 15% concentration were prepared with these polyvinyl amino-acetals. The polyvinyl amino-acetal (5) was also mixed with the original polyvinyl alcohol to prepare aqueous solutions (6) and (7) of an average degree of amino-acetalization of 2.2% and 2.8%, respectively, and also an aqueous solution (8) with polyvinyl alcohol alone was prepared for purposes of comparison, each solution having a polymer concentration of 15%. These solutions were extruded through a spinneret having 600 holes into a bath containing an aqueous solution of saturated sodium sulphate at 45° C. After a bath travel of 1.5 m. the coagulated yarn was removed from the coagulating bath, passed between glass guides and further stretched to a draw ratio 1.5/1 between rollers; the yarn had then about 3 x 600 drs. The thus spun yarn was subjected to a heat-treatment in air at 220° C. for 1 minute while its length was kept constant. The yarn was then formalized in an aqueous solution containing 15% of sulphuric acid, 15% of sodium sulphate, and 5% formaldehyde at 70° C. until the degree of formalization amounted to about 35%. The properties of the filaments thus obtained are shown in the following table: Dye-absorption is shown by the dye bath exhaustion when dyed with 2% Acid Scarlet 3R and 2% sulphuric acid, at 1:50 of liquor ratio and at 80° C. for 1 hour.

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
Average degree of amino-acetalization (mol. percent).	0.5	1.2	2.2	3.8	5.2	2.2	3.8	0
Polyvinyl alcohol content in polymer blend (percent).	0	0	0	0	0	57	26	100
Wet softening temperature after heat-treatment (° C.).	60	48	Dissolved at 30° C.	Dissolved at 20° C.	Dissolved at 20° C.	85	51	92
Average degree of amino-acetalization after formalization (mol. percent).	0.5	1.1	Gelated	Gelated	Gelated	2.0	3.5	0
Shrinkage in boiling water after 30 min. (percent).	53	48				3.5	55	1.0
Softening temperature in air (° C.)	170	148				215	180	218
Dye-absorption at 80° C. (percent)	85	100 (fiber sticky)				100	100	0
Dry tenacity (g./d.)	3.1	2.6				3.7	3.2	3.9

Example 2

Polyvinyl alcohol as in Example 1 was used and amino-acetalized in aqueous solutions containing 6% of polyvinyl alcohol, 5% of sulphuric acid and (1) 1.5%, (2) 3.0%, (3) 5.0% and (4) 15% of beta-cyclohexylamino-butyraldehyde-dimethylacetal respectively at 70° C. for 5 hours (with exception of 30 hours for (4)). After the reaction, the solutions were subjected to dialysis and formed into films. The polyvinyl amino-acetals thus obtained had amino-acetalization degrees of (1) 9.0%, (2) 17%, (3) 25%, and (4) 52%, respectively. Various polymer blends of these polyvinyl amino-acetals and the original polyvinyl alcohol were spun in the same manner

as Example 1 and subjected to heat-treatment and formalization. The results are shown in the following table:

Amino-acetalization degree of polyvinyl amino-acetal (mol. percent)	9.0		17		25		52	
Average degree of amino-acetalization (mol. percent)	6.8	2.5	5.1	2.5	2.5	0.5	12.0	7.5
Polyvinyl alcohol content in polymer blend (percent)	22	69	64	82	86	97	64	76
Wet softening temperature after heat-treatment (° C.)	20	88	71	90	91	93	57	68
Average degree of amino-acetalization after formalization (mol. percent)	6.6	2.4	4.9	2.4	2.3	0.5	11.2	6.8
Shrinkage in boiling water after 30 min. (percent)	46	3.8	6.2	3.0	3.0	2.2	22	8.1
Softening temperature in air (° C.)	138	211	209	216	218	217	175	182
Dye-absorption at 80° C. (percent)	100	100	100	100	100	72	100	100
Dry tenacity (g./d.)	2.4	3.6	3.4	3.8	3.8	4.0	2.7	3.2

Example 3

Using polyvinyl alcohol as in Example 1, the reaction product amino-acetalized in an aqueous solution containing 6 g. of polyvinyl alcohol, 6 g. of sulphuric acid, and 4.7 g. of β-cylcohexylamino-propionaldehyde-diethylacetal at 70° C. for 10 hours had an amino-acetalization degree of 28.2%. After the reaction, the solution was neutralized to a pH of about 6 by slowly adding thereto dropwise an aqueous solution of 1% sodium hydroxide. To this solution were added 54 g. of the original polyvinyl alcohol and dissolved therein by heating to prepare a solution containing the polymer blend in a a concentration of 15%, and 2.1% of sodium sulphate, the polyvinyl alcohol content in this polymer blend being 84.5%. This solution was spun by extruding through a spinneret having 300 holes into a coagulating bath containing 350 g./l. of sodium sulphate and 0.2 g./l. of sulphuric acid at 45° C. The coagulated yarn travelled through a bath length of 1.5 m., was taken out and stretched to a draw ratio of 3/1 between positively driven rolls, then introduced into a second bath containing 200 g./l. of sodium sulphate at 70° C. to stretch further to a draw ratio of 2/1, and finally wound up on a bobbin. The thus obtained oriented yarn was drawn in air of 240° C. to a ratio of 3/1 for 1 second and then heat-treated in air of 250° C. for 1 second keeping its length constant. The yarn was then wound into skeins, which were treated in an aqeous solution containing 18% of sulphuric acid, 10% of sodium sulphate and 5% of formaldehyde at 70° C. for 2 hours.

This filament had an average degree of amino-acetalization of 2.4%, and a degree of formalization of 48%; if treated in hot water of 110° C. for 30 minutes, the shrinkage was 3.0%; the softening temperature in air was 223° C., and the dry tenacity 6.8 g./d. This filament was substantially pure white and its dye absorption was 100% under dyeing conditions as set forth in Example 1.

Example 4

Polyvinyl alcohol prepared as in Example 1 was treated at 70° C. for 48 hours in an aqueous solution containing 6% of polyvinyl alcohol, 15% of phosphoric acid and 2.5% of amino-acetaldehyde-dimethylacetal. The solution was then dialyzed, and the water was evaporated. The obtained chips of polyvinyl aminoacetal had a degree of amino-acetalization of 27.5%. These chips were blended with the original polyvinyl alcohol at the ratio of 1:10, and aqueous solutions were prepared having the following compositions:

(1) An aqueous solution containing 13% of the polymer blend, and

(2) An aqueous solution containing 13% of the polymer blend and 2% of sodium sulphate.

These solutions were spun by extruding through a spinneret having 2000 holes into a saturated aqueous solution of sodium sulphate at 50° C. After a bath travel of 3 m. the filaments were stretched by glass guides and rollers. The filaments were heat-treated (*a*) in air of 230° C., (*b*) in nitrogen of 230° C., and (*c*) in water vapor of 220° C. under 1 atmospheric pressure for 2 minutes, respectively, while keeping the length constant. With respect to the extent of yellowing of the heat-set filaments, there was almost no difference between (1) and (2), while (*a*) was strongly yellowed, whereas (*b*) and (*c*) were not discolored. The wet softening temperatures of the fiaments after heat-set were 78–80° C. and almost no difference was shown. These filaments were subjected to benzalization in an aqueous solution containing 3% of sulphuric acid, 1.5% of benzaldehyde and 0.5% of sodium dibutyl naphthalene sulfonate at 60° C. for 1 hour. All the filaments thus obtained resisted to boiling water and their softening temperatures in air were higher than 190° C., and they showed complete dye exhaustion under the same dyeing conditions, but without sulphuric acid, as set forth in Example 1. They also showed good dye-ability with direct dyes; for example, the dye absorption was 95–100% when they were dyed with Congo-red 2% at 80° C. for 1 hour. On microscopic inspection, it was found that the cross section is kidney-shape for (1), while that of (2) is nearly round.

On the other hand, benzalized filaments prepared in the same manner as (1)–(*a*) using polyvinyl alcohol alone showed a zero dye absorption with acid dyestuffs and an absorption of 2% with direct dyestuffs.

Example 5

By adding 0.01 part of 2,2'-azobisisobutylonitrile to a solution consisting of 70 parts of vinyl acetate and 30 parts of methanol, and polymerizing at 60° C. for 10 hours, polyvinyl acetate was prepared, which was converted by complete hydrolysis into polyvinyl alcohol of a polymerization degree of 1200.

Said polyvinyl alcohol was reacted in aqueous solutions containing 6% of polyvinyl alcohol, 5.5% of sulphuric acid and various concentrations of beta-cyclohexylaminobutyraldehyde-diethylacetal at 70° C. for 8 hours, respectively, and the reacted solutions were subjected to dialysis and converted to films.

The concentrations of the amino-acetal used and the degrees of amino-acetalization of the obtained polyvinyl aminoacetal were as follows:

	Conc. of amino-acetal, percent	Degree of amino-acetalization, percent
(1)	0.35	2.1
(2)	0.9	5.3
(3)	2.1	12.4

These films were dissolved with the original polyvinyl-alcohol to prepare aqueous solutions for dry spinning as defined in the table below.

The concentration of polymer blends was in all cases 45%. The solutions were extruded downwardly through a spinneret having 5 holes into a cell of 5 m. length, the temperature at a point spaced 1 m. from the top of the cell being about 140° C. The filaments coming out of the cell were continuously cold drawn to a draw ratio of 3/1 and wound up. Then the filaments were drawn in

Wood's metal to a ratio of 3.5/1 at 210° C. during 1 second and were shrunk by about 10% at 220° C. during 1 second. The filaments were then acetalized in an aqueous solution containing 3% of hydrochloric acid, 10% of sodium chloride and 2% of formaldehyde at 50° C. for 1 hour. The properties of the filaments thus obtained are shown in the following table:

	(1)	(2)	(3)		(4)
Degree of amino-acetalization of polyvinyl amino-acetal (mol. percent)	2.1	5.3	12.4		0
Average degree of amino-acetalization in polymer blend (mol. percent)	1.0	1.0	0.3	1.0	0
Polyvinylalcohol content in polymer blend (percent)	52	80	97	91	100
Wet softening temperature after heat-treatment (° C.)	66	82	97	86	99
Average degree of amino-acetalization after formalization (mol. percent)	0.9	0.8	0.3	0.9	0
Shrinkage in boiling water after 30 min. (percent)	8.6	5.8	1.8	2.3	2.1
Softening temperature in air (° C.)	192	205	215	210	219
Dye absorption at 80° C. (percent)	100	98	63	87	0

Example 6

A polyvinyl alcohol-ethylene copolymer containing about 3% of ethylene and obtained by substantially complete hydrolysis of the corresponding polyvinyl acetate-ethylene copolymer was amino-acetalized under the following conditions:

Copolymer	5%.
Hydrochloric acid	4%.
Gamma-amino-butyraldehyde-dimethylacetal	1.55%.
Water	89.45%.
Temperature	70° C.
Duration	6 hours.

The solution was dialyzed and prepared into a film which had a amino-acetalization degree of 20%. Said film was dissolved together with the original copolymer in a ratio of 1:9 and with sodium hypophosphite to an aqueous solution containing 17% of the polymer blend and 1% of sodium hypophosphite.

This solution was wet spun into an aqueous solution containing 300 g./l. of sodium sulphate and 50 g./l. of sodium chloride at 35° C. under stretching by means of guides. After spinning, the filaments were cut to lengths of about 10 cm. and subjected in the free state to a heat-treatment in air of 220° C. for 5 minutes. The filaments were crimped, the number of crimps per cm. being 9, and the wet softening temperature was 77° C. The fibers were then acetalized in an aqueous solution containing 3% of hydrochloric acid, 30% of methyl alcohol and 2% of isovaleraldehyde at 70° C. for 1 hour. The thus obtained fibers had resistance to boiling water and showed 100% dye absorption under the same conditions as described in Example 1. The color of the fibers was light yellowish. When sodium hypophosphite was not added to the spinning solution in this example, the filaments had a dark yellow color.

If in this example the polymer blend containing polyvinyl amino-acetal was not used and the same treatment was carried out with polyvinyl alcohol-ethylene copolymer alone, the fibers obtained could not be dyed under the same dyeing conditions.

Example 7

Polyvinylalcohol prepared as in Example 1 was reacted in an aqueous solution containing 6% of polyvinyl alcohol, 5.5% of sulphuric acid, and 8% of beta-hydrazino-propionaldehyde-dimethylacetal at 70° C. for 8 hours. By dialyzing the reaction mixture and evaporating water, a polyvinyl amino-acetal resin having an amino-acetalization degree of 30.1% was obtained. This resin was dissolved with the original polyvinyl alcohol at the ratio of 1:10 to prepare an aqueous solution of 15% polymer blend, which solution was extruded through a spinneret having 100 holes into an aqueous solution of saturated sodium sulphate at 50° C. After a bath travel of 3 m. the spun filaments were subjected to stretching by means of guides and rollers, and drawn in air of 230° C. to 160% of their original length for 5 seconds and heat-set in air of 235° C. for 10 seconds by keeping the length constant. The filaments were then treated in an aqueous solution containing 5% of formaldehyde, 12% of sulphuric acid, and 15% of sodium sulphate at 70° C. for 1 hour. The filaments thus obtained are resistant to boiling water; their average degree of amino-acetalization was 2.3% and the degree of formalization was 32%. The dye absorption of the filaments was 100% if dyed under the same conditions as in Example 1.

Example 8

Polyvinyl alcohol prepared as in Example 1 was reacted in an aqueous solution containing 5% of polyvinyl alcohol, 10.1% of sulphuric acid and 1.55% of alpha-piperidino-methyl-1.3-dioxolane at 70° C. for 20 hours; the obtained polyvinyl amino-acetal had an amino-acetalization degree of 12.3%. The reacted solution was dialyzed, and polyvinyl alcohol was added in an amount 4 times that used in the amino-acetalization step; then an aqueous 14% solution of said polymer blend was prepared. This aqueous solution was wet-spun under the same conditions as in Example 7 and the filaments thus obtained were drawn in air at 235° C. to a ratio of 3/1 for 5 seconds and then shrunk to about 15% in air at 240° C. for 10 seconds. After the filaments had been treated in an aqueous solution containing 5% of formaldehyde, 15% of sulphuric acid and 15% of sodium sulphate at 70° C. for 1 hour, their average amino-acetalization degree was 2.1% and their formalization degree 38%. The shrinkage was 2.0% when treated in hot water of 110° C. for 30 minutes. The dye absorption was 100% under the same dyeing conditions as in Example 1.

Example 9

Polyvinyl alcohol obtained as in Example 5 was reacted in an aqueous solution containing 6% of the polyvinyl alcohol, 15% of hypophosphorous acid and 8% of beta-(2-methyl-4-ethyl-piperdino)-butyraldehyde diethylacetal at 70° C. for 15 hours. Subsequently, the reaction mixture was dialyzed and water was evaporated to form a film. The degree of amino-acetalization of this film was 35%. 116 g. of this film and 640 g. of the original polyvinyl alcohol were dissolved in water and an aqueous solution of 15% of the polymer blend was prepared. This aqueous solution was spun by extrusion through a spinneret having 600 holes into a saturated aqueous solution of sodium sulphate at 47° C. After a bath travel of 1.5 m., the filaments were subjected to stretch by means of guides and rolls. The thus spun filaments were drawn to a ratio of 1.5/1 in air at 230° C. for 30 seconds, and shrunk to 15% in air at 235° C. for 30 seconds. Then the filaments were treated in an aqueous solution containing 2.0% of o-chloro-benzaldehyde, 4% of sulphuric acid and 0.5% of laurylammonium trimethylchloride at 70° C. for 1 hour. The filaments thus obtained were resistant to boiling water, and their softening temperature in air was higher than 200° C. If dyed under the same dyeing condition as in Example 1 (but at a temperature of 95° C.), the dyestuff from the dye-bath was perfectly absorbed.

Example 10

Polyvinyl alcohol obtained as in Example 5 was reacted in aqueous solution containing 6% of the polyvinyl alcohol, 5.5% of sulphuric acid and 4.5% of delta-morpholinovaleraldehyde-dimethylacetal at 70° C. for 12 hours. The mixture was dialyzed, and polyvinyl alcohol in an amount of 10 times that of the polyvinyl alcohol used in the amino-acetalization step was added, and the concentration of the polymer blend in the aqueous solu-

tion was adjusted at 15%. This aqueous solution was wet spun under the same conditions as in Example 7. The spun filaments were drawn to a ratio of 2/1 for 10 seconds in air at 220° C. and shrunk to 20% for 10 seconds in air at 225° C. The filaments were treated in an aqueous solution containing 5% of formaldehyde, 12% of sulphuric acid and 15% of sodium sulphate at 70° C. for one hour. The average degree of amino-acetalization of the filaments was 2.5% and the degree of formalization was 34%. The shrinkage of the filaments when treated in hot water of 110° C. for 30 minutes, was 4.3%. The dye absorption of the filaments was 100% if dyed under the same dyeing conditions as in Example 1.

Example 11

A reaction mixture containing 60 g. of polyvinyl alcohol obtained as in Example 5, 100 g. of 98% sulphuric acid, 13.5 g. gamma-pyridine aldehyde and 826.5 g. of water was heated at 70° C. for 15 hours under stirring; the obtained polyvinyl amino-acetal had an amino-acetalization degree of 18.1%. The mixture was then dialyzed and 540 g. of the original polyvinyl alcohol and 84 g. of sodium sulphate were added to the solution; the concentration of the polymer blend in said solution was adjusted to 14%. This aqueous solution was spun under the same conditions as in Example 7. The filaments thus obtained had almost circular cross-section.

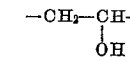
The filaments were drawn in air at 235° C. to a ratio of 2.8/1 for 5 seconds and heat-set in air at 240° C. for 10 seconds, keeping the length constant.

Afterwards the filaments were treated in an aqueous solution containing 5% of formaldehyde, 15% of sulphuric acid and 15% of sodium sulphate at 70° C. for 1 hour. The filaments thus obtained were resistant to boiling water and had an average amino-acetalization degree of 1.65% and a formalization degree of 35%. The dye absorption was 100% if dyed under the same conditions as in Example 1.

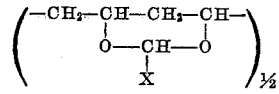
For the purposes of comparison, the following table shows the shrinkage in boiling water for 30 minutes and dye absorption at dyeing of 80° C. which were observed with oriented, animalized polyvinyl alcohol fibers made by wet spinning aqueous solutions containing 15% of a polymer blend consisting of polyvinyl alcohol and polyvinyl amino-acetal into a saturated aqueous solution of sodium sulphate, heat-treating at 220° C. for 2 minutes in air, thereby keeping the length constant, and then formalizing in an aqueous solution containing 15% of sulphuric acid, 15% of sodium sulphate and 5% of formaldehyde at 70° C. for 1 hour.

What we claim is:

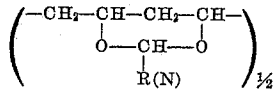
1. An oriented synthetic linear polymeric filament consisting of polymer blend of polyvinyl nonamino-acetal which consists of vinyl alcohol



units and nonamino-acetalized vinyl alcohol



units wherein X is a monovalent radical having 1 to 19 carbon atoms and no basic nitrogen atoms, and polyvinyl non-amino-and amino-acetal which consists of vinyl alcohol units, non-amino-acetalized vinyl alcohol units and amino-acetalized vinyl alcohol



units wherein R(N) is a monovalent radical having 1 to 3 basic nitrogen atoms and 1 to 20 carbon atoms, said polymer blend consisting to the extent of at least 30% by weight, of polyvinyl nonamino-acetal, the ratio of amino-acetalized vinyl alcohol units to the sum of total vinyl alcohol units and total nonamino-acetalized vinyl alcohol units being between 1:499 and 1:9, and the ratio of total nonamino-acetalized vinyl alcohol units to the sum of total vinyl alcohol units and amino-acetalized vinyl alcohol units being betwen 1:19 and 1:0.67, said filament having a wet softening temperature, at which the filament shrinks by 10% of its original length when immersed in water for 30 minutes, of at least 100° C. and a dye absorption of at least 30% when said filament is dyed at 80° C. with Acid Scarlet 3R (C.I. No. 185) of 2%, based on the weight of the filament.

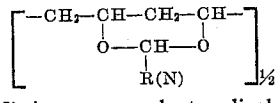
2. An oriented synthetic linear polymeric filament consisting of a polymer blend of

(1) at least 30% by weight of acetalized polyvinyl alcohol consisting of vinyl alcohol units and vinyl alcohol units acetalized by reaction with a nonamino-mono aldehyde having 1 to 20 carbon atoms, said acetalized polyvinyl alcohol being free of basic nitrogen-containing groups, and

(2) amino-acetalized polyvinyl alcohol consisting of vinyl alcohol units, acetalized vinyl alcohol units free of basic nitrogen-containing groups which units are acetalized by reaction with a nonamino-mono aldehyde having 1 to

Amino-aldehyde of amino-aldehyde-dimethylacetal used	Average degree of amino-acetalization in polymer blend (mol. percent)	Content of polyvinyl-alcohol in polymer blend (percent)	Degree of formalization (mol. (percent)	Shrinkage in boiling water for 30 min. (percent)	Dye absorption at 80° C. (percent)
Cyclohexylamino-acetaldehyde	1.75	91.0	43.3	1.5	100
N-benzylamino-acetaldehyde	1.00	75.0	39.5	1.3	88
p-Dimethylamino-benzaldehyde	1.80	90.0	43.1	2.0	100
Diethylamino-acetaldehyde	2.30	91.0	43.2	5.8	100
B-piperidino-propionaldehyde	1.30	89.0	38.3	3.0	95
B-phenylethylamino-propionaldehyde	2.50	90.5	45.1	5.7	100
B-amino-propionaldehyde	3.10	91.7	47.5	3.1	100
B-amino-butyraldehyde	3.50	89.0	49.4	4.1	100
B-benzylamino-butyraldehyde	2.70	91.0	46.5	3.5	100
N-aminoethyl-cyclohexylamino-acetaldehyde	1.00	83.3	43.1	2.7	100
N-aminomethylamino-propionaldehyde	0.90	85.0	40.2	3.3	99
B-(B-ethylamino-ethyl)-thiopropionaldehyde	0.50	80.0	38.0	2.1	80
p-Carboxymethyl-amino-o-chlorobenzaldehyde	2.20	91.5	45.8	3.3	100
B-ethylamino-butyraldehyde	3.00	90.7	50.1	4.8	100
B-methylamino-propionaldehyde	1.40	93.3	39.7	3.6	98
(B-methylamino-ethyl-thio)-acetaldehyde	1.30	90.0	40.8	4.2	98
B-cyclohexylamino-butyraldehyde	2.50	92.8	47.3	5.1	100
B-cyclohexylamino-propionaldehyde	2.60	90.1	49.2	4.9	100
Amino-acetaldehyde	1.90	87.7	40.5	3.8	100
Control (no amino-acetal used)	0	100	34	1.2	0

20 carbon atoms, and amino-acetalized vinyl alcohol units,

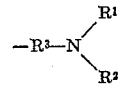


wherein —R(N) is a monovalent radical having 1 to 3 basic nitrogen atoms and 1 to 20 carbon atoms,

the ratio of amino-acetalized vinyl alcohol units to the sum of the total vinyl alcohol units and acetalized vinyl alcohol units which are free of basic nitrogen-containing groups in the said polymer blend being in the range of 1:499 to 1:9,

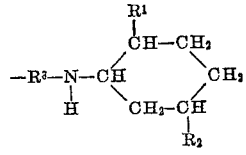
the ratio of acetalized vinyl alcohol units free of basic nitrogen-containing groups to the sum of the total vinyl alcohol units and amino-acetalized vinyl alcohol units in the said blend being in the range of 1:19 to 1:0.67, said filament having a wet softening temperature, at which the filament shrinks by 10% of its original length when immersed in water for 30 minutes, of at least 100° C. and a dye absorption of at least 30% when said filament is dyed at 80° C. with Acid Scarlet 3R (C.I. No. 185) of 2% based on the weight of the filament.

3. The filament as defined in claim 2 wherein —R(N) is



R^1 and R^2 being monovalent radicals selected from the group consisting of hydrogen and alkyl groups having not more than five carbon atoms, and —R^3— being an aliphatic divalent radical having 1 to 4 carbon atoms.

4. The filament as defined in claim 2 wherein —R(N) is

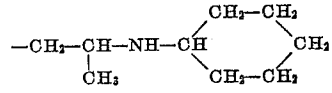


R^1 and R^2 being monovalent radicals selected from the group consisting of hydrogen and alkyl groups having not more than five carbon atoms, and R^3 being an aliphatic divalent radical having 1 to 4 carbon atoms.

5. The filament as defined in claim 2 wherein —R(N) is R^3—(N^1), R^3 being an aliphatic divalent radical having 1 to 4 carbon atoms and (N^1) being a heterocyclic nitrogen base.

6. The filament as defined in claim 2 wherein —R(N) is —R^3—$NH.NH_2$, —R^3— being an aliphatic divalent radical having 1 to 4 carbon atoms.

7. The filament as defined in claim 2 wherein —R(N) is



and the nonamino-monoaldehyde is formaldehyde.

No references cited.

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,992,204 July 11, 1961

Tetsuro Osugi et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 5, line 29, for "conditions" read -- condition --; column 11, line 67, for "8%" read -- 3% --; column 12, line 43, for "-piperdino)-" read -- -piperidino)- --; column 13, line 1, for "at" read -- to --; column 14, line 32, for "betwen" read -- between --.

Signed and sealed this 21st day of November 1961.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents

USCOMM-DC