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Jamison et al.

[11] **3,742,104**

[45] **June 26, 1973**

[54] **PRODUCTION OF SHAPED SYNTHETIC ARTICLES HAVING IMPROVED DYEABILITY**

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[21] Appl. No.: **33,180**

Related U.S. Application Data

[63] Continuation of Ser. No. 481,587, Aug. 23, 1965, abandoned.

[52] **U.S. Cl.** ..... **264/78**, 8/130.1, 8/173, 264/184, 264/210 F, 264/343

[51] **Int. Cl.** **D01d 5/12**, D01f 3/10

[58] **Field of Search** 264/344, 78, 342, 264/343, 210, 184; 8/130.1, 137, 173

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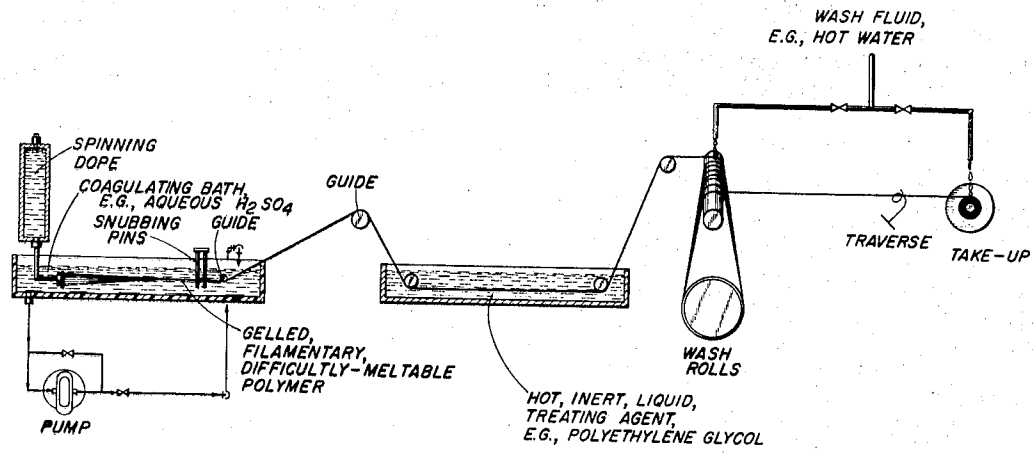
[57] **ABSTRACT**

A chemical relaxation treatment for increasing dyeability of wet spun difficultly meltable filamentary material such as high melting polyamides, polyurethanes and polyureas which filaments are spun from a concentrated sulfuric acid solution and coagulated in an aqueous sulfuric acid bath. The residual sulfuric acid contained in the filamentary material is subsequently activated to increase the dyeability of the resulting product.

4 Claims, 3 Drawing Figures



3 Sheets-Sheet 1

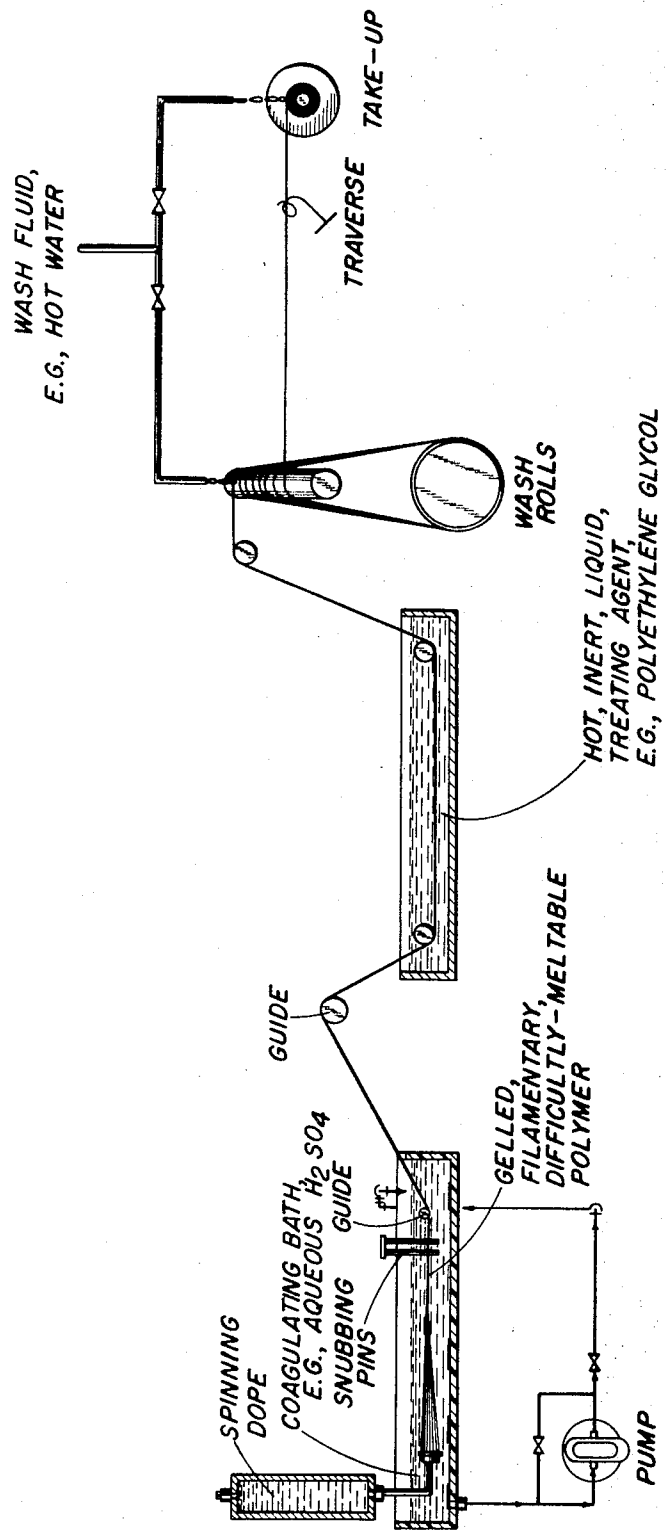


FIG-1

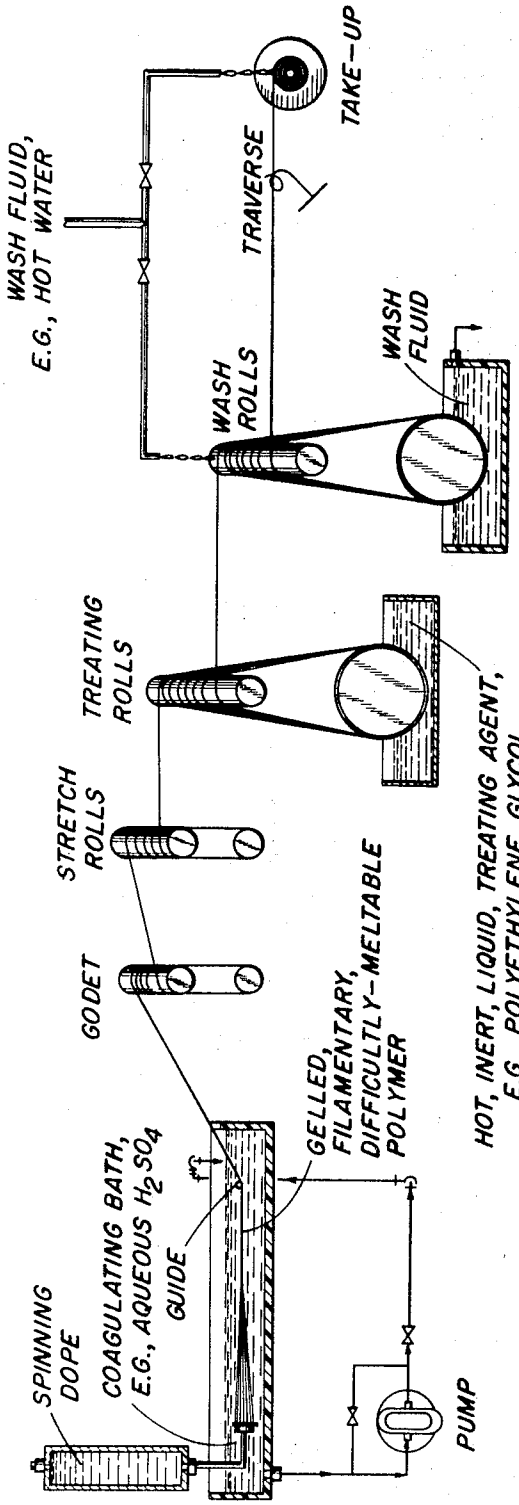

TAKE-UP
TRAVERSE
WASH FLUID, E.G., HOT WATER
WASH ROLLS
WASH FLUID
TREATING ROLLS
STRETCH ROLLS
GODET
HOT, INERT, LIQUID, TREATING AGENT, E.G., POLYETHYLENE GLYCOL
GELLED, FILAMENTARY, DIFFICULTLY-MELTABLE POLYMER
SPINNING DOPE
COAGULATING BATH, E.G., AQUEOUS H_2SO_4
GUIDE
PUMP

FIG. 2

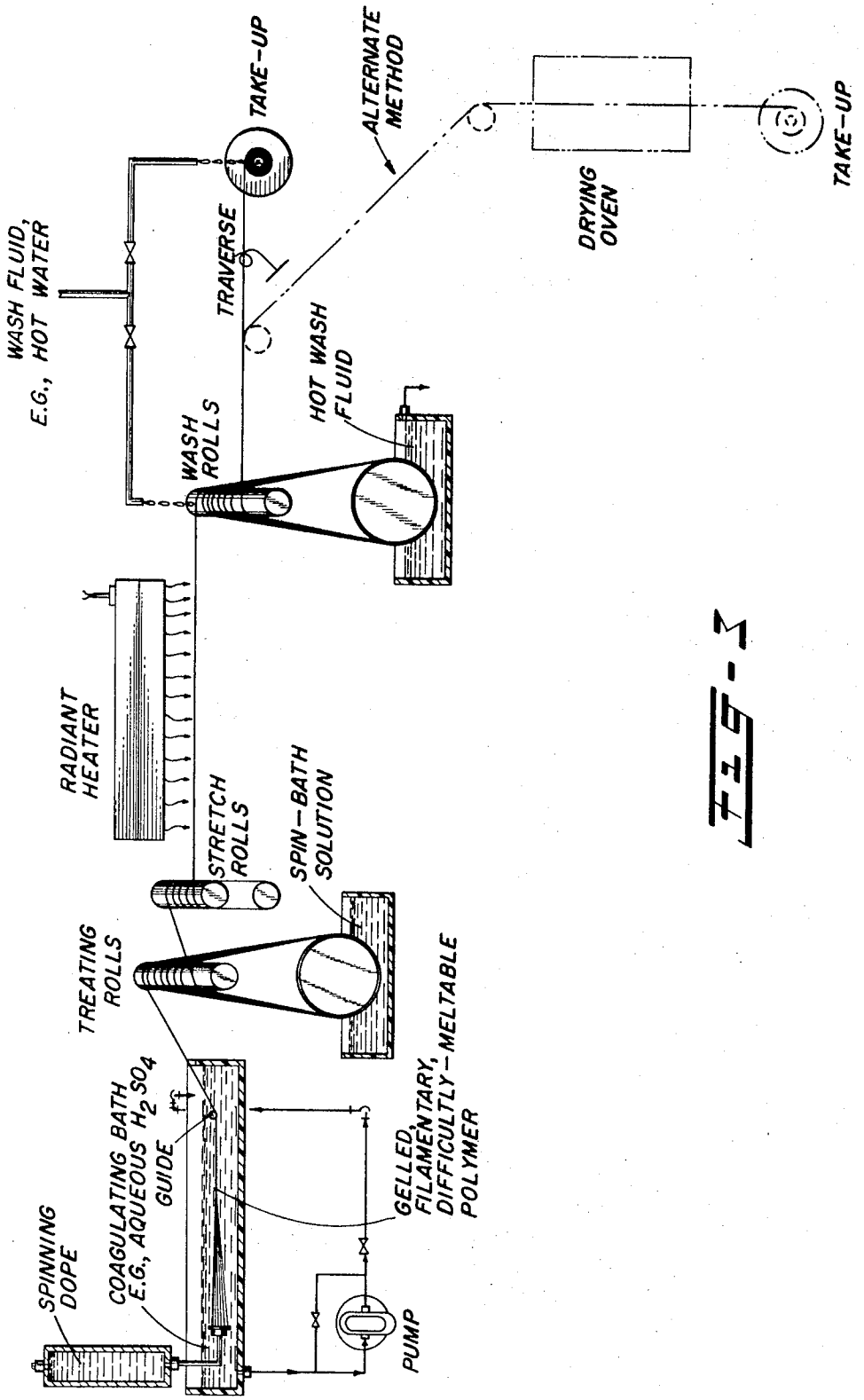

TAKE-UP
ALTERNATE METHOD
DRYING OVEN
TAKE-UP
WASH FLUID, E.G., HOT WATER
TRAVERSE
HOT WASH FLUID
WASH ROLLS
RADIANT HEATER
STRETCH ROLLS
SPIN-BATH SOLUTION
TREATING ROLLS
COAGULATING BATH E.G., AQUEOUS H_2SO_4
GUIDE
SPINNING DOPE
GELLED, FILAMENTARY, DIFFICULTLY-MELTABLE POLYMER
PUMP

FIG-1

PRODUCTION OF SHAPED SYNTHETIC ARTICLES HAVING IMPROVED DYEABILITY

This invention which is a continuation application of copending application, Ser. No. 481,587, filed Aug. 23, 1965, now abandoned relates broadly to the production of shaped articles and, more particularly, shaped synthetic articles having improved dyeability.

Still more particularly the invention is concerned with a method of preparing a particular class of shaped synthetic articles in film, fiber or other form. This class includes shaped, wet-formed difficultly-meltable polymers, especially fiber-forming (fiber-formable) condensation polymers having nitrogen and/or oxygen atoms, and preferably both nitrogen and oxygen atoms, as a part of the polymer chain. More specific examples of such condensation polymers are the high-melting polycarbonamides, particularly those melting above 275°C. such as polyhexamethylene terephthalamide.

By "difficultly-meltable" polymers such as used herein are meant polymers that cannot be shaped easily using melt-extrusion techniques because they tend to degrade materially and/or to polymerize further to a useless, infusible mass when heated sufficiently to melt them.

It was known prior to the present invention that polymers to which this invention is applicable could be formed into shaped articles, specifically filaments or fibers. See, for example, U.S. Pats. Nos. 3,154,512 and 612 of Parczewski; 3,154,609-Cipriani; 3,154,610-Denyes; and 3,154,613-Epstein et al., each dated Oct. 27, 1964; and 3,179,618-Roberts, dated Apr. 20, 1965.

In the aforementioned U.S. Pats. Nos. 3,154,609, 610 and 613 it is disclosed that condensation polymers of the kind with which this invention is concerned can be dissolved in sulfuric acid containing at least 75 percent by weight of H_2SO_4 and that the resulting solution can be extruded through an opening of predetermined cross-section having at least one thin dimension into a liquid coagulating or spin bath of aqueous sulfuric acid having an acid concentration lower than that of the sulfuric acid in which the polymer was dissolved and such that the polymer is coagulated into a shaped article, e.g., a filamentary material, in gel state.

The present invention is especially concerned with means for increasing the dyeability of the final product, more particularly by activating the aqueous sulfuric acid contained in the shaped article, e.g., filamentary material (especially oriented filamentary material) thereby to improve the dyeability, including acid and disperse dyeability, of the washed and dried article or material.

Various ways may be employed to secure effective activation of the aqueous sulfuric acid contained in the gelled filamentary material or other shaped article. For example, various liquid media may be used for this purpose. (By "liquid" media are meant treating agents that are in liquid state at the treating temperature; they may be non-liquids, e.g., solids or semi-solids, at ambient temperature.) The media employed should provide effective thermal contact for activation of the aqueous sulfuric acid contained in the gelled structure. Additionally, the available evidence indicates that water-miscibility and a low rate of diffusion of the liquid treating agent into the gelled body are desirable characteristics of effective liquid media.

Examples of the aforementioned treating or activating agents are polyethers having the recurring unit represented by the formula

$$+O—R+_n O—$$

I

wherein R represents a divalent organic radical, more particularly a divalent hydrocarbon radical, and n is a number such that the average molecular weight of the polymer is within the range of from about 500 to about 10,000. Preferably the polyethers embraced by Formula I are those which are water-soluble or miscible.

Thus, we may use as the treating agent in practicing this invention polyoxyalkylene polyols having an average molecular weight within the range of from about 500 to about 10,000 such as those available from Wyandotte Chemicals Corporation, Wyandotte, Michigan, under the names of PLURACOL V-5 and V-7.

More specific examples of treating agents that may be employed are those represented by the general formula

$$ROCH_2(CH_2OCH_2)_nCH_2OR'$$

II

wherein R and R′ each represent a member of the group consisting of hydrogen and monovalent organic radicals, more particularly monovalent hydrocarbon radicals, and n is a number such that the compound has an average molecular weight within the range of from about 500 to about 10,000. Preferably the hydrocarbon radicals embraced by the definitions of R and R′, and which may be the same or different, are either a lower alkyl radical containing not more than seven carbon atoms, e.g., methyl, ethyl, and propyl through heptyl radicals (both normal and isomeric forms); or a phenyl or tolyl radical; or a benzyl radical.

When R and R′ in Formula II each represent a hydrogen atom, the compound is a polyethylene glycol which may be represented by the general formula

$$HOCH_2(CH_2OCH_2)_nCH_2OH$$

III

wherein n has the same meaning as given above with reference to Formula II.

Other examples of treating or activating agents that may be employed include chlorinated hydrocarbons such as compounds that are commercially available under the name of Arochlors (chlorinated diphenyls); aromatic ethers such as diphenyl ether, methyl phenyl ether, ethyl phenyl ether, the ditolyl ethers, etc; and high-boiling, straight-chain alcohols such as lauryl alcohol and others of the homologous series which, when not soluble in water, are soluble in organic solvents, e.g., ethanol, and hence can be washed from the gelled article.

The treating agents used in carrying the present invention into effect, including those mentioned above by way of illustration, are members of the class of substances that properly may be described as being inert (substantially completely inert), heating (or heat-transfer) media. This is indicated by the fact that some beneficial effect in improving the dye-receptivity of the final product is obtained by the use of heat alone, as is more fully described later herein.

The treating or activating agents employed are preferably those having an atmospheric boiling point or range of boiling points not lower than about 150°C., or, more preferably, not lower than about 175°C.; additionally, as indicated hereinbefore, it is preferred that the treating agent have at least some miscibility with, or solubility in, water or in an aqueous solution of sulfuric acid. Preferably, too, the treating agent is one which is immiscible with the polymer. It is also preferred to use a treating or relaxation agent that does not have any appreciable vapor pressure at the treating temperature; and this is especially true with respect to certain chlorinated compounds the vapors of which might have unfavorable physiological effects upon the operators.

It is not essential that the treating agent be one that has at least some solubility in water so long as it is soluble in some organic solvent whereby the excess agent can be washed from the treated acid-laden gelled article. However, the use of such a non-aqueous washing fluid adds to the cost of the process unless it is an inexpensive or a by-product fluid medium that may also serve some other useful function concurrently with the washing operation.

Another technique for activating the aqueous sulfuric acid contained in the gelled article, e.g., gelled filamentary material, is to heat the acid-laden structure after it has been removed from the coagulating bath and while it is traveling through air. For example, after orienting the molecules of a gelled filamentary material along the fiber axis by stretching between stretch rolls, the aqueous sulfuric acid contained in the oriented gelled filaments is activated, before washing the latter, by heating the said filamentary material at a temperature of from about 40°C. to about 100°C., preferably not higher than about 90°C., for a period sufficient to increase the dyeability of the final product. The resulting heat-treated filamentary material is treated, as by washing, to remove the sulfuric acid, followed by drying.

The novel features of our invention are set forth in the appended claims. The invention itself, however, will be most readily understood from the following description taken in connection with the accompanying drawing, which is illustrative of the invention, and wherein

FIG. 1 illustrates schematically one embodiment of the invention;

FIG. 2 illustrates schematically another embodiment of the invention; and

FIG. 3 illustrates schematically still another embodiment of the invention.

THE POLYMERIC MATERIAL

The polymers that are wet-formed into filamentary or other shaped structures or bodies and then treated in accordance with this invention to improve their dyeability are difficultly meltable, fiber-forming polymers. Preferably the treatment is applied to those polymers having repeating =NCO— groups, more particularly -NRCO- groups where R represents hydrogen or a monovalent organic radical, e.g., a hydrocarbon radical such as a lower-alkyl radical. Such polymers include the difficultly meltable polyamides such as those wherein the —NRCO— groups are attached to carbon atoms on each side; the polyurethanes which contain repeating =NCOO— groups, more particularly —NRCOO— groups; the polyureas which contain repeating =NCON= groups, more particularly —RNCONR— groups, and similar condensation polymers.

There is no particular advantage in wet-forming, e.g., wet-spinning, many of the polymers of the classes broadly described in the preceding paragraph, more particularly those which are adapted to be melt-extruded through orifices, slots or other shaped openings to form the shaped body. However, in the case of the high-melting or difficultly meltable polymers, such polymers must be wet-spun rather than melt-spun. Wet-spinning often leads to voids that adversely affect certain properties, e.g., dyeability of the spun filaments of yarn. The present invention is one solution to this problem. It provides practical means for altering and/or aiding in the alteration of the internal structure of the polymer so as to remove such voids thereby to improve the dyeability, luster and other useful and desirable properties of the article; and, especially, to do so as a step in a continuous process.

Thus, the technique of the instant invention is most useful when applied to shaped articles formed of high-melting polymers, more particularly those melting above 210°C. and especially above 275°C.; polyurethanes and polyureas melting above 179°C., especially above 210°C.; and, in general, polymers having cyclic groups such as 1,4-cyclohexylene and/or heterocyclic groups such as piperazylene or an alkyl-substituted piperazylene group, e.g., 2-(lower-alkyl) piperazylene such as 2,6-dimethylpiperazylene, as an integral part of the polymer molecule.

Some contemplated polyamides are, for example, those having repeating structural units of the formula

—NR—Y—NR'—CO—Y'—CO—

that result from the condensation of a dicarboxylic acid or a derivative thereof, e.g., a salt, acyl halide, or ester of such an acid, with a diamine, wherein the R's, which may be the same or different, are hydrogen or monovalent organic radicals, e.g., lower-alkyl radicals such as methyl or ethyl, and the Y's, which also may be the same or different, are divalent organic radicals such as alkylene, e.g., ethylene, tetramethylene or hexamethylene, arylene such as para- and meta-phenylene, para- and meta-xylene, and para- and meta-diethylenebenzene, cycloalkylene such as 1, 4-cyclohexylene and divalent heterocyclic radicals such as those derived from piperazine, and monoalkyl- and dialkylpiperazines, e.g., 2-methyl- and 2,5-dimethylpiperazines and 2-ethyl- and 2,5-diethylpiperazines, wherein the open bonds are attached to the nitrogen atoms, and wherein the chemical structure of the polymer and/or the polymerization technique used is such that a relatively high-melting polymer is obtained.

An important group of polyamides within the above group, and to which the present invention is especially applicable in treating shaped articles wet-formed therefrom, includes those in which Y and/or Y' is or contains a para- or metaphenylene radical or a 1,4-cyclohexylene radical. Particularly important are condensation products of a diamine and terephthalic acid or a derivative of terephthalic acid, e.g., tere-phthalyl chloride or a dialkyl terephthalate. Some specific polymers within this latter group are poly(polymethylene) terephthalamides wherein the polymethylene groups contain from two to 10 carbon atoms, inclusive, e.g., polyhexamethylene terephthalamide, polyoctamethylene terephthalamide, polytetramethylene terephthal-

amide, polyethylene terephthalamide, and polypiperazylene terephthalamide. Other polyterephthalamides are poly(o-, m-, and p-phenylene) terephthalamides, poly(o-, m-, and p-xylylene) terephthalamides and poly(o-, m-, and p-diethylenephenylene) terephthalamides, the latter produced, for example, by condensing an ester-forming derivative of terephthalic acid with para-bis(beta-aminoethyl) benzene.

The treatment of this invention is applicable in the production of filaments and other shaped articles of high-melting polyamides of aromatic acids other than terephthalic acid, e.g., of isophthalic acid, 2,6-naphthalenedicarboxylic acid, p,p'-dicarboxydiphenyl, (p,p' -dicarboxydiphenyl) methane, phenylenediacetic acid, phenylenedipropionic acid, and phenylenedibutyric acid. The diamine moieties of these other aromatic carboxylic acids may be the same as in the aforementioned polyterephthalamides. Illustrative, then, of polyamides other than the polyterephthalamides are the polyisophthalamides, especially polyethylene isophthalamide. The treatment of the present invention also may be employed in making shaped bodies from high-melting polyamides resulting from a condensation reaction between (a) alkylene dicarboxylic acids such as adipic acid and (b) cyclic diamines such as p-xylene diamine and p-bis(amino-ethylbenzene).

Also contemplated is the treatment of shaped, high-melting, autocondensation polymers (e.g., those melting above 275°C.) of an aminocarboxylic acid or a lactam or other derivative of such an acid, which polymers have repeating structural units of the formula —N-R—Y—CO— wherein R and Y are as defined above. Some specific polyamides melting above 275°C. within this group are polymers of the following: 1-carboxymethyl-4-aminocyclohexane or its lactam, 1-carboxy-4-aminocyclohexane or its lactam and 1-carboxymethyl-3-aminocyclopentane or its lactam.

Polyurethanes that may be wet-formed and treated in accordance with this invention are polymers having repeating structural units of the formula

—NR—Y—NR'—CO—O—Y'—CO—O—

and resulting, for example, from the condensation of a diisocyanate with a dihydric alcohol or phenol or the condensation of a diamine with a bis(chloroformate) of a dihydric alcohol or phenol, where the R's and Y's are as described above in connection with the polyamides, and the chemical structure of the polymer and/or the polymerization techniques used are such that a polymer melting above 179°C., preferably above 210°C., is obtained. Particularly useful in practicing this invention are polyurethanes prepared from dihydric alcohols or phenols containing a meta- or para-phenylene or a 1,4-cyclohexylene radical. Some specific, shaped polyurethanes which may thus be treated are the condensation product of piperazine with the bis(chloroformate) of bis(p-hydroxyphenyl)-propane-2,2, the condensation product or piperazine with the bis(chloroformate) of hydroquinone and the condensation product of tetramethylene diamine with the bis(chloroformate) of butanediol-1,4, each of which has a melting point above 210°C.

Polyureas that may be wet-formed and subjected to the treatment of this invention include those having repeating structural units of the formula

—CO—NR—Y—NR—CO—NR'—Y'—NR'—

wherein the R's and Y's are as defined above. They may be synthesized, for example, by the addition of a diisocyanate to a diamine, the condensation of a diurethane with a diamine, the condensation of a carbon oxyhalide such as phosgene with a diamine, or by heating an alpha,beta-diurea with a diamine, the chemical structure of the polymer and/or the polymerization technique being such that a polymer melting above 170°C., preferably above 210°C., is obtained. Some specific polyureas that may be employed in practicing this invention are those obtained from the reaction of hexamethylene diisocyanate with hexamethylene diamine and from the reaction of m-pheynlene diisocyanate with m-phenylene diamine, each of which polyurea melts above 210°C.

The polymer-containing solvent solutions or dopes which are prepared and extruded to produce a shaped article are preferably made by dissolving the polymer in sulfuric acid containing at least 75 percent, more particularly at least 80 percent, by weight of H_2SO_4. Preferably, too, the sulfuric acid is concentrated sulfuric acid containing 95 to 100 percent by weight of H_2SO_4. Fuming sulfuric acid, e.g., such acid containing up to 6 or 7 percent by weight or even higher of free SO_3, also may be employed. A suitable concentration of polymer in the dope is in the range of, for example, from 5 to 30 percent by weight.

The use of solvents for the difficultly meltable condensation polymer other than sulfuric acid is not precluded. For example, instead of using sulfuric acid as a solvent, one may employ a solvent containing over 85 percent by weight of phosphoric acid (see U.S. Pat. No. 3,154,612, *supra*); or a solvent comprising at least 70 percent by weight of antimony trichloride and formic acid or acetic acid as a diluent in an amount up to 30 percent by weight of the solvent (see U.S. Pat. No. 3,154,512, *supra*).

The liquid coagulant or spin-bath composition is a liquid in which the solvent employed to dissolve the polymer is soluble but in which the polymer is insoluble. Generally it is desirable to use, as the liquid coagulant, a liquid containing a lower concentration of the same solvating agent employed in making the polymer solution, said lower concentration being such that the polymer is coagulated into a gelled structure such as a sheet, film, tape, ribbon, band, rod, tube, bar, cylinder, monofilaments, multifilaments (including tow), and the like. Thus, when the solvent in which the polymer is dissolved is sulfuric acid containing at least 75 percent, or at least 80 percent, by weight of H_2SO_4, the liquid coagulating bath is preferably aqueous sulfuric acid having a concentration of H_2SO_4 lower than that of the sulfuric acid in which the polymer is dissolved and, as aforementioned, such that the solution of the polymer is coagulated into the form of a gelled structure or body.

When using the preferred liquid coagulant, i.e., aqueous sulfuric acid, the concentration of sulfuric acid in said liquid coagulant may be varied considerably depending upon, for example, the particular technique employed in activating the aqueous sulfuric acid contained in the gelled material and/or other modifications of the process and/or the properties other than improved dyeability that are wanted in the final product. However, such acid concentration, especially when

wet-forming polyterephthalamides such as polyhexamethylene terephthalamide, i.e., poly(hexamethyleneterephthalamide), may be below about 60 percent by weight H_2SO_4, e.g., from 0 percent to 50 percent. By "0 percent" it is meant that water alone is the liquid coagulant into which the sulfuric acid solution of the polymer is extruded to form the gelled structure, the liquid coagulant then becoming acidified with H_2SO_4 as it extracts this acid from the gelled structure during passage of the latter through the liquid coagulating bath.

When gelled films (especialy such films which yield a transparent film as a final product) are to be prepared, the use of lower sulfuric acid concentration of the liquid coagulant, for example below about 40% H_2SO_4, more particularly within the range of from 0 percent to 30 or 35 percent H_2SO_4, are conducive to the formation of thicker films if and when desired.

The temperature of the coagulating bath may be varied as desired or as may be required depending for example, upon the particular polymer employed, the particular solvent used to dissolve the polymer, the particular liquid coagulant used, the extrusion rate, the particular properties desired in the final product, and other influencing factors. Thus, the bath temperature may range, for example, from room temperature (20°–30°C.) to about 100°C., but preferably is within the range of from about 40°C. to about 60°C. When necessary, heating coils or other sources of heat may be provided in order to maintain the coagulating bath at the desired temperature above ambient temperature.

In the embodiment of the invention illustrated in FIG. 1 and which shows one technique for making filamentary material, the gelled filaments are continuously pulled through the coagulating bath. However, while in the coagulating bath the filaments are brought into contact with at least two, smooth, curved surfaces which are so positioned with respect to each other, and with respect to the direction of travel of the moving filamentary material, that the said filamentary material is caused to so reverse its direction that its angle of bend is at least about 40°. Thus, the angle of bend or snubbing angle in effecting orientation of filamentary material may be within the range of from about 40° to about 120°, more particularly from about 60°to 90°, e.g., 60°, 70°, 80° or 90°. In similarly orienting films, the snubbing angle may be up to 180°.

The smooth, curved surfaces to which reference has been made in the preceding paragraph may take the form of two rods or pins that are so positioned as to provide the aforementioned angle of bend. Such rods or pins may be formed of, or at least surfaced with, a smooth, hard, wear-resistant surface such as those that are commercially available under such names as Alsimag (and which is understood to be an aluminum magnesium silicate), Heanium (mainly Al_2O_3), and the like.

The rods or pins mentioned in the preceding paragraph may be disposed in the coagulating bath so that they extend vertically downwardly into the bath of liquid coagulant. Since the amount of tension imposed upon the filamentary material (for the same rod or pin diameter) is dependent upon the relative orientation of the rods, it is desirable to mount both rods upon a common head. Such a head may take the form of a fork mechanism for mounting a pair of rods as is shown in the copending application of one of us (Saunders E. Jamison), Ser. No. 233,827, filed Oct. 29, 1962, and assigned to the same assignee as the present invention. Thus, by merely rotating a shaft to which is attached a mounting head carrying the two rods in spaced relationship, the said two rods can be readily disposed at the desired angular position with regard to the direction of travel of the gelled filamentary material.

With regard to the foregoing comment concerning the amount of tension imposed upon the filamentary material by the rods or pins, it may be further mentioned that the amount or degree of tension exerted by such rods or pins is proportional to the friction imposed upon the moving filamentary material and that the latter, in turn, depends upon the contact distance. Hence the diameter of the snubbing pin or rod is important. In the technique herein described with reference to the angle of bend or snubbing angle of the moving filaments, the diameter of the pin or rod over which the filamentary material was passed, when calculating the snubbing angle, was one-fourth inch. Consequently, it is to be understood that in the description herein given with reference to the angle of bend of the moving filamentary material, the stated angle of bend provides friction or tension corresponding to that obtained when the moving filamentary material is passed, at the specified angle of bend, over a rod or pin one-fourth inch in diameter.

It is not essential that the rods or pins extend vertically downwardly into the bath of liquid coagulant. Thus, if desired, they may be positioned horizontally in the coagulating bath.

Also, it is not essential that one use stationary rods or pins in the coagulating bath as tension-inducing members positioned to provide the desired angle of bend. For example, a pair of positively driven rotating rolls may be utilized. Such rolls are each rotated at the same speed, which speed is less than that of the take-up roll. Accordingly, by winding the gelled filamentary material about each of such rotating rolls positioned in the coagulating bath and about the take-up roll, more or less tension (as desired or as conditions may require) can be imposed upon the filamentary material while it is in the coagulating bath. The amount of induced tension can be controlled by varying the differential in speed of rotation between the pair of such rollers in the bath of liquid coagulant and the take-up roll.

After being oriented by snubbing in the coagulating bath as described above, the oriented filamentary material is withdrawn from the coagulating bath by any suitable means and contacted with a liquid medium or a plurality of different liquid media which are effective in activating the aqueous sulfuric acid retained or held by the oriented, gelled filamentary material. The concentration of the H_2SO_4 in the solvent in which the polymer is dissolved to form the spinning dope, the concentration of the H_2SO_4 in the spin bath, the temperature of the said bath and the distance the coagulated filaments are led through the bath before being withdrawn therefrom are preferably so adjusted that the concentration of H_2SO_4 in the aqueous sulfuric acid retained by the filamentary material when it is removed from the bath is within the range of, by weight, from 51 to 58 percent, preferably from 54 to 57 percent, thereof.

From the spin bath the oriented filamentary material is led over guide or skew rolls, or any other suitable guide means, to a liquid treating means for activation of the aforesaid H_2SO_4 retained by the filamentary ma-

terial. The liquid activating agent or treating medium may be applied to the filamentary material by any suitable means, e.g., while it is continuously moving in a helical path over a pair of converging or skew rolls; or, as shown in FIG. 1, by passage through a bath of the liquid treating agent.

The general characteristics of liquid media that are useful as activators of the aqueous sulfuric acid retained by the gelled material in filamentary or other form have been given hereinbefore. Particularly useful are the polyethylene glycols (polymers of ethylene oxide). Typical properties of the latter compounds, which are commercially available, are the following:

Carbowax® polyethylene glycol	Average molecular weight	Sp. Gv., 20/20° C.	Melting range, ° C.	Viscosity cks., 210° F.	Solubility, percent by weight in water
600	570-630	1.130	20-25	10.5	Complete.
1,000	950-1,050		36.5-39.5	17.4	About 70.
1,500	500-600	[1] 1.151	38.0-41.0	13-18	About 73.
1,540	1,300-1,600	1.15	43.0-46.0	25-32	About 70.
4,000	3,000-3,700	[1] 1.204	53.0-56.0	75-85	About 62.
6,000	6,000-7,500		60.0-63.0	700-900	About 50.

[1] Density, g. per ml. 20° C.

NOTE.—Carbowax is a trademark for Union Carbide Corporation's brand of polyethylene glycols. The above and other polyethylene glycols are more fully described in Booklet F-7658C of Union Carbide Chemicals Company, 270 Park Avenue, New York 17, N.Y.

In general, the application temperatures (i.e., the temperature at which the treating agent is applied to the gelled material) are within the range of from about 50°C. up to a temperature just below (e.g., about 5° or 10°C. below) the temperature of incipient softening of the polymer. Usually, the upper temperature limit is not higher than about 150°C. In all cases the temperature employed is such as will convert the treating agent to liquid state if it is not initially in such state.

The period of time that the treating agent remains in contact with the shaped polymer in gel state, under the particular temperature conditions employed, is in all cases sufficient to improve the useful and desirable properties, especially dye-receptivity, of the treated material. It is difficult to state this time period with exact precision since there are so many different variables that may influence it. These include the constitution of the polymer being treated, its denier if in filamentary form or its thickness if in film, sheet or other form, the particular wet-forming technique employed, the temperature at which the treating agent is applied, the particular concentration of H_2SO_4 in the aqueous sulfuric acid retained by the gelled polymeric material being treated, and other influencing factors.

For obvious reasons, it is desirable that the time and temperature employed in applying the liquid treating agent, and the concentration of H_2SO_4 in the aqueous sulfuric acid retained by the gelled body undergoing treatment, are not such as will result in excessive softening of the shaped polymer, and especially when the latter is in the form of multifilamentary material. Such excessive softening can lead to coalescence (i.e., sticking or fusing together) of the individual filaments, which is undesirable.

The available evidence indicates that the contact time at the application temperature should, for optimum results, be sufficient to result in a rapid and efficient transfer of heat from the treating agent to substantially all of the aqueous sulfuric acid retained by the shaped, gelled polymer. At treating temperatures within the range of about 50°–150°C., this time is usually less than 5 minutes. The time will vary depending upon the particular temperature employed within this range; the internal structure (e.g., size, arrangement and number of voids in the structure) of the particular gelled polymer being treated; the viscosity of the treating agent at the treating temperature and its degree of miscibility with water; and other influencing factors. For example, at higher temperatures approaching the point of incipient softening of the gelled polymer and when the treating agent employed has a relatively low viscosity at the treating temperature, it may be necessary to limit the time of the treatment to one-fourth second or lower (that is, to cause it to occur almost instantaneously) in order to avoid or minimize fiber coalescence.

The upper time limit of the application temperature is critical only to the extent that it should not be so long that the sulfuric acid in the gelled material during the treatment adversely affects the useful properties of the final product. For instance, as has previously been indicated, the time should not be so long as to result in excessive (if any) coalescence of individual filaments of a multifilamentary material. The maximum treating time in some cases may be as long as 12 to 24 hours, or even 2 or 3 days or more, provided that there are no adverse effects such as an objectionable decrease in tensile strength, failure to obtain optimum improvement in dyeability (especially with acid and disperse dyes), discoloration, loss of luster, and the like.

The liquid treating or activating agent, together with any aqueous sulfuric acid that may still be retained by the gelled, shaped polymer in filamentary or other form, is removed from the gelled structure by any suitable means. For example, washing may be effected while the gelled material, especially when it is a filamentary structure, is passing in a helical path over a pair or a plurality of pairs of wash rolls or reels. Or, a wash trough or vessel, as illustrated in FIG. 1, or a series of wash troughs or vessels through which the unwashed, treated, gelled material passes, may be employed. Preferably, the unwashed material passes countercurrently to the flow of the washing fluid.

The washing fluid may be water alone or a combination of water and other washing fluids in different permutations. For example, an initial wash with water may be followed at a second station by an alkaline wash (e.g., a water solution of ammonia, or an aqueous solution of sodium or potassium carbonate or bicarbonate), followed by another water wash at a third station; or the alkaline wash may be applied first followed by a water wash and then by a wash with a more volatile wash fluid than water, e.g., acetone, methanol, ethanol or the like. Any desired or required number of wash stations may be employed to remove the excess acid and/or activating agent from the treated, gelled material, e.g., 1,2 or 3 through 10 stations, or more, if necessary.

The washed, gelled material is then dried by any suitable means either before or after collection on a take-up roll. In many cases, passage of the gelled structure (particularly if in film form) through air at room temperature causes the film to dry sufficiently for take-up (without sticking of contacting layers on the roll), espe-

cially if a volatile solvent such as acetone or methanol has been applied as a final wash before take-up, and the time of exposure to air has been sufficiently long to volatilize substantially all of the solvent. Washed films also may be dried by, for example, passing the film through a drying zone such as a heated oven while held on a support. Preferably washed, gelled, filaments, sheets, films and other elongated structures of continuous (i.e., indefinite) length are dried by passage over the warm or hot (up to about 130°C.) surfaces of a heated roll. Where discoloration under heat may be objectionable, e.g., in the production of thin transparent films, drying at an elevated temperature is preferably done in a non-oxidizing atmosphere, e.g., nitrogen, helium, argon, etc.

Instead of using snubbing pins as illustrated in FIG. 1 to effect orientation of the freshly spun, gelled or coagulated filaments, the filamentary material may be passed over a guide and led out of the coagulating bath for stretching between rolls as illustrated in FIG. 2. (Draw ratios in practicing this invention are preferably below 4.0, e.g., from 2.5 to 3.8.) The stretched filamentary material is then contacted with a hot liquid treating agent as hereinbefore described with reference to FIG. 1, e.g., by passing through a bath of such a treating fluid. Or, the treating agent may be applied as illustrated in FIG. 2 and wherein the gelled yarn or filamentary material is advanced over skewed rolls, the lower of which is partly immersed in a trough of the hot treating agent.

The treated filamentary material is then washed as previously has been described with reference to FIG. 1. For example, it may be washed as illustrated in FIG. 2 using skewed rolls and a trough containing water or other washing fluid as mentioned in the preceding paragraph with reference to the application of the treating agent. The treated and washed material is then dried as hereinbefore described.

Another technique for activating the aqueous sulfuric acid contained in the gelled filamentary material does not necessitate the use of a hot liquid activating agent. This embodiment of the invention, which is illustrated in FIG. 3, merely involves heat-treatment of the acid-laden gelled structure. For example, the gelled material after leaving the coagulating bath may be heated while passing through air or other gaseous medium to a temperature within the range of from about 40°C. to about 100°C., preferably not higher than about 90° or 95°C. This technique is especially applicable when the gelled material has been oriented by snubbing in the coagulating bath as previously has been described. Alternatively, orientation by stretching as shown in FIGS. 2 and 3 may be employed.

The procedure illustrated in FIG. 3 involves passing the shaped, gelled structure such as a yarn bundle to several sets of skewed rolls, the lower roll of the first set of which dips in a trough containing spin-bath solution, more particularly aqueous sulfuric acid having a concentration of H_2SO_4 of about 50 weight percent. The second set of rolls is operated at approximately the take-up speed, its excess in speed over that of the first pair providing the principal stretching factor for orientation of the fibers. Washing is begun with passage of the yarn over the third pair of rolls. Heat is applied by any suitable means to the yarn while it is passing between the stretch and the wash rolls. For example, heating may be effected with a radiant source of heat such as electrical heating coils, infra-red lamps, etc. A further increase in the dyeability of the final product is obtained by heating the continuously moving filamentary material or the like while it is in relaxed or untensioned state, or merely under a low tension only sufficient to keep the filaments mvoing in a continuous path. This can be done, for instance, by heating the gelled material while the wash rolls are operating at a speed somewhat below that of the stretch rolls.

The washing fluids and the washing techniques employed may be the same as has been described above with reference to the embodiments of the invention illustrated in FIGS. 1 and 2. Advantageously washing is effected by applying the washing fluid to the upper (or upon both upper and lower) of a pair of skewed rolls as the gelled material, e.g., a continuous length of gelled filaments, is moving in a helical path over the surfaces of the rolls; or, as illustrated in FIG. 3, by having the lower of a pair of skewed rolls partly immersed in a bath of the washing fluid.

The washed, gelled yarn or the like may be collected in gel state on a take-up roll as illustrated in FIG. 3 and then subsequently dried by any suitable means. Or, if desired, and as illustrated by the phantom view in FIG. 3, the gelled yarn may be taken directly from the wash rolls to drying means. The drying means may take the form of, for example, heated drying rolls over which the gelled yarn is continuously passed; or a drying oven, tube or hot slot which is internally and/or externally heated by any suitable means may be employed. Alternatively, drying may be effected merely by exposure to air at ambient temperature for a prolonged period or for a shorter period of time in warm air, after which the dried yarn is collected on a take-up roll. Lubricating and/or antistatic and/or other finishes may be applied to the yarn before, after or both before and after drying the yarn or other shaped article.

From the foregoing description it will be noted that a solvent solution or dope is prepared by dissolving a difficultly meltable condensation polymer in a concentrated solution of sulfuric acid; and that this dope is then coagulated into a gelled, shaped article by extrusion through a shaped orifice into a coagulating bath having a lower concentration of sulfuric acid than that used in dissolving the polymer. At the face of the extrusion orifice(s) or spinneret the concentration of H_2SO_4 in the aqueous sulfuric acid retained by the freshly coagulated shaped article, e.g., filamentary material, is much higher than it is at its point of exit from the coagulating bath. In practicing the present invention optimum results are obtained in improving the dye-receptivity of the final product by withdrawing the yarn or the like from the bath at that point in the bath where the gelled yarn contains a concentration of sulfuric acid that makes it effective as a treating agent for chemically relaxing the yarn, more particularly from 51 to 58 percent H_2SO_4 and preferably from 54 to 57 percent H_2SO_4.

The addition of the treating or activating agent (inert heating medium) used in practicing this invention to the gelled yarn at the stage of acid concentration in the yarn that was mentioned in the preceding paragraph makes the yarn more tractable. In other words, it makes the yarn more amenable to the action of acid of the most effective concentration from the standpoint of time and temperature required to relax the yarn and thereby improve the dyeability of the final product.

The process of the present invention is then, in effect, a two-stage coagulation process wherein the initially bound coagulant comprised of aqueous sulfuric acid is activated (reactivated) with the result that the internal structure of the polymer is altered or modified in a manner whereby the dye-receptivity of the final product is improved; and, specifically, a more readily dyed filamentary material or film is obtained.

In order that those skilled in the art may better understand how the present invention can be carried into effect, the following examples are given by way of illustration and not by way of limitation. All parts and percentages are by weight unless otherwise stated.

EXAMPLE 1

An extrudable solution having a Synchro-Electric viscosity at 25°C. of about 5,000 poises, is made from the following:

	Parts
Polyhexamethylene terephthalamide	10.8
Sulfuric acid, 98 percent	83.0
Ammonium sulfate	6.2

The ammonium sulfate is added to the concentrated sulfuric acid at room temperature (20°–30°C.), and the mixture is stirred at the same temperature until the ammonium sulfate goes into solution. The polyhexamethylene terephthalamide in finely divided state is added to, and admixed with, the solution of ammonium sulfate in the sulfuric acid. Mixing is effected at about 40°–50°C., and is continued until the polymer has substantially completely dissolved, e.g., for about 2 hours. The polymer component of this solution has an inherent viscosity (I.V.) of about 2.0 measured as a solution of 0.4 gram of polymer per deciliter of concentrated sulfuric acid solvent at 25°C.

A dope bomb under nitrogen pressure is used in feeding the above-described dope, after deaeration and filtration, through a platinum spinneret with 40 holes of 0.10 mm. diameter into a liquid coagulating bath consisting of sulfuric acid at 50°C. This coagulating bath is circulated through a rectangular trough formed of clear poly(methyl methacrylate) by an external Jabsco pump equipped with a bypass. Constant temperature in the coagulating bath is maintained with a glass-enclosed electric heater and a glass-enclosed thermoregulator.

Snubbing pins for effecting orientation of the gelled filamentary material are positioned vertically in the bath from above. The pins are comprised of a pair of one-fourth inch Alsimag rods held five-eighths inch between centers in a 2-hole rubber stopper which is fixed in a clamp above the bath. The stopper is rotated to provide the desired snubbing angle, specifically 60°, 70°, 80° and 90° in this example.

After passing through the coagulating bath for a distance of about 38 inches the oriented, gelled yarn is continuously removed from the bath to a pair of skewed rolls (2 inches in diameter), the speed of which is adjusted by means of Heller or Graham drive systems. These rolls function primarily as guide rolls and as means for drawing the yarn past the snubbing pins and out of the coagulating bath.

After passing over the aforementioned skewed rolls, the yarn is passed to a small stainless steel trough containing hot (about 120°C.) polyethylene glycol having an average molecular weight of 570–630, specifically CARBOWAX 600. The yarn is immersed in this bath of treating or activating agent for a distance of 16 inches. The take-up speed is such that the yarn has a residence time in the bath of about 0.8 second. The "control" yarns, that is, gelled yarns containing aqueous sulfuric acid from the coagulating bath, by-pass the above-described bath of polyethylene glycol.

Yarn to which the treating agent has been applied is led from the treatment bath through a traversing mechanism to a perforated Viscose-type take-up bobbin where it is wound at 30 meters per minute under a cascade of hot tap water. The hot tap water removes nearly all of the polyethylene glycol and most of the sulfuric acid. The bobbin of yarn is then washed completely free of H_2SO_4 by immersion for about 16 hours in cold, running, tap water. Thereafter it is dried in air at room temperature.

Instead of washing and drying the yarn as described above, it may be washed and dried by any other means or combination of means such as those illustrated in FIGS. 1, 2 and 3 or by other means described earlier in this specification.

The properties and dyeability measurements of treated and control yarns obtained at various concentrations of H_2SO_4 in the coagulating bath and at various snubbing angles are given in Table I. The dyeability values given in this table represent the percent up-take on the weight of the fiber (i.e., owf) of the acid dye, Alizarine Sky Blue BS-CF (C.I. No. Acid Blue 78). from an "infinite" dye bath in 3 hours at 95°C. and at a pH of 3. By "infinite" dye bath it is meant that the amount of the dye is more than 100 times the weight of the fiber.

It will be noted from the data given in this table that the increase in dyeability of the treated yarn is from 2.2 to over 4.3 times that of the untreated yarn and with, in most cases, only a minor decrease in fiber tenacity. Such results were wholly unobvious and in no way could have been predicted.

TABLE I

Conc. of H_2SO_4 in spin bath, percent	Snubbing angle, degrees	Treated with polyethylene glycol	Den./fil.	Elongation, percent	Tenacity, g./d.	Dye uptake, percent OWF
48.5	90	No	1.8	21	5.9	0.5
48.5	90	Yes	1.9	20	5.4	1.1
48.5	70	No	1.8	29	4.9	0.8
48.5	70	Yes	1.8	32	4.7	2.1
50.7	80	No	1.9	29	5.3	0.6
50.7	80	Yes	1.7	23	5.6	1.8
50.6	70	No	1.7	30	5.3	0.7
50.6	70	Yes	1.7	26	5.3	2.3
50.7	60	No	1.7	38	4.5	0.9
50.7	60	Yes	1.7	40	4.5	3.4
51.8	70	No	1.7	46	4.5	0.9
51.8	70	Yes	1.7	28	4.0	3.9

EXAMPLE 2

Essentially the same procedure is followed as described under Example 1 with the exception that the polymer employed in making the spinning dope is polyhexamethylene terephthalamide having an I.V. of 1.9, and 11.6 percent thereof is used instead of 10.8 percent as in Example 1.

The dope is extruded through the above-described 40-hole spinneret into a coagulating bath consisting of aqueous sulfuric acid having an H_2SO_4 concentration of 50.0 percent. The coagulating bath is maintained at 50°C., and the snubbing pins are arranged at an angle

of 70°. The treating or activating agent employed is a commercially available polyoxyalkylene polyol, *viz.*, *PLURACOL V–7* (produced and sold by Wyandotte Chemicals Corporation, Wyandotte, Michigan). It has an average molecular weight within the range hereinbefore mentioned. The bath of polyethylene glycol is maintained at a temperature of about 95°C. instead of 120°C. as in Example 1.

The properties and dyeability values for the control and the treated yarns are tabulated below:

Yarn	Filament Denier	Tenacity g./d	Elongation %	Dye* Up-take % owf
Control	1.8	5.7	24	0.5
Treated	1.8	5.2	21	1.9

*An acid dye, specifically Alizarine Sky-Blue BS-CF, as in Example 1.

When the control and treated yarns are dyed with a disperse dye, specifically Eastone Red N-GLF (C.I. No. Disperse Red 35), the dye up-take of the treated yarn is more than twice that of the control yarn.

EXAMPLE 3

The same procedure is followed as described in Example 2 with the exception that, instead of using snubbing pins in the coagulating bath to orient the gelled yarn as in Examples 1 and 2, the said pins are omitted and the yarn is oriented by stretching between stretch rolls as is illustrated in FIG. 2. As there shown, the coagulated yarn is led out of the spin bath under a guide roll to a godet in the form of a pair of 2-inch rolls and then to a pair of stretch rolls, also 2 inches n diameter. in stretch rolls are operated at a peripheral speed sufficiently faster than the godet so as to provide a draw ratio of about 3.0.

The stretch-oriented yarn is then treated with a polyoxyalkylene polyol as in Example 2, washed and dried. A control yarn is processed in the same way with the exception that the treatment rolls shown in FIG. 2 are by-passed. The control and treated yarns are then tested for dye-receptivity to both acid and disperse dyes as in Example 2. With both acid and disperse dyes the dye up-take of the treated yarn is from 2 to 3 times that of the control yarn.

EXAMPLE 4

This example illustrates a technique for activating the aqueous sulfuric acid retained by a gelled structure formed from a condensation polymer of the kind used in this invention without using an inert liquid activating agent. More particularly, the procedure is essentially the same as that illustrated in FIG 3.

A spinning dope prepared as described under Example 2 is extruded through a spinneret having 5,040 holes, each with a diameter of 0.10 mm., into a trough containing a spin-bath solution of 49.8 percent H_2SO_4 at 45°C. In the trough, the gelled yarn bundle or tow is passed through a tube, having a length of 120 inches and an inside diameter of 3 inches, to the first of a set of skew rolls as illustrated in FIG. 3, and thence to final take-up at a speed of 50 meters per minute.

The first set of rolls dips into a trough containing spin-bath solution having a concentration of 49.8 percent H_2SO_4. These rolls are operated at a peripheral speed considerably lower than the take-up speed. The second set of rolls is operated at approximately the take-up speed, except as indicated below. The excess in speed of the second pair of rolls over that of the first pair provides the principal stretching factor for effecting orientation of the fibers. Washing is begun, as indicated in FIG. 3, with passage of the yarn over the third pair of rolls.

Application of heat, specifically by means of infrared lamps, to the bundle of filaments as it passes between the stretch and wash rolls increases the dye-receptivity of the filamentary material. This improvement in dyeability is further enhanced by reducing the wash-roll speed somewhat below the speed of the stretch rolls. The temperature of the unwashed, stretched yarn is increased from about 25°C. to about 40°C. by the heat treatment.

In this example the dye up-take is measured in a finite bath containing the acid dyestuff Alizarine Sky Blue BS-CF in the amount of 4 percent by weight of the fiber sample. More detailed data and results are given in Table II.

TABLE II

Sample No.	Percent stretch	Percent shrinkage—stretch to wash	Heated after stretching	Fiber properties: Ten., g./d.	Elong., percent	Dye up-take, percent OWF
1	180	None	No	4.5	32	2.0
2	180	None	Yes	4.4	26	2.4
3	180	10	No	3.9	42	2.2
4	180	10	Yes	4.0	40	2.9

Instead of using polyhexamethylene terephthalamide in making dope solutions from which are produced filamentary materials and other shaped articles having improved dye-receptivity in accordance with the present invention, one may similarly make and treat shaped articles of the polyisophthalamides, e.g., polyethylene isophthalamide, polyhexamethylene isophthalamide, or of any other difficultly meltable polymer of the kind with which this invention is concerned and of which numerous examples have been given hereinbefore both broadly and specifically.

It is to be understood that the foregoing detailed description is given merely by way of illustration and that many variations may be made therein without departing from the spirit of the invention.

What is claimed is:

1. A method for producing polyamide fibers comprising:

A wet-spinning a solvent solution of a difficultly meltable, filament-forming, poly(polymethylene)-terephthalamide polymer through a shaped orifice into a liquid coagulating bath in which the said polymer is insoluble thereby to obtain a filamentary material in gel state,

the solvent in which the said polymer is dissolved being sulfuric acid containing at least 75 percent by weight of H_2SO_4, and

the liquid coagulating bath into which the said solvent is extruded being aqueous sulfuric acid having a concentration lower than that of the sulfuric acid in which the polymer is dissolved and such that the solution of the polymer is coagulated into the form of a gelled, filamentary material containing residual sulfuric acid;

B orienting the molecules of the gelled filamentary material by stretching;

C subsequently activating the aqueous sulfuric acid in the oriented filamentary material, before washing the latter, by heating the said filamentary material at a temperature of from about 40°C. to about

100°C. in an aqueous solution of polyethylene glycol for a period sufficient to increase the dyeability of the final product;

D washing the resulting heat-treated filamentary material to remove the excess sulfuric acid; and

E drying the washed filamentary material.

2. A method as in claim 1 wherein the aqueous sulfuric acid contained in the oriented filamentary material is activated by contacting the said filamentary material with hot, liquid polyethylene glycol represented by the general formula

$$HOCH_2(CH_2OCH_2)_nCH_2OH$$

where n is a number such that the average molecular weight of the said polyethylene glycol is within the range of from about 500 to about 10,000.

3. The method as in claim 1 wherein the polymer is a polymer melting above 275°C.

4. The method as in claim 1 wherein the poly(-polymethylene) terephthalamide is polyhexamethylene terephthalamide.

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