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FORMATION OF WET SPUN FIBERS

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This invention relates to a novel process of forming wet spun fibers and to a novel coagulation bath for such fibers. More particularly, it relates to the use of an organosiloxane-oxyalkylene block copolymer as a wet-spinning aid in the formation of wet spun fibers.

In the wet spinning process for the production of polymeric filaments, a solution of a polymer or polymer derivative in some convenient solvent is extruded through a spinnerette into a solution capable of coagulating the polymer or polymer derivative into a solid filament form which is then removed from the coagulating bath for subsequent processing. In the usual methods of fiber production, spinnerettes having multiple openings are used. When the filaments emerge from the several orifices, they are initially kept separate from each other by the coagulating bath. They may subsequently come in contact with each other in the coagulating bath or at a guide over which they are carried. Unless the coagulation and hardening of the filaments has progressed sufficiently before this occurs, then contact between filaments can result in adhesion of several filaments together. Generally, this is undesirable since the resulting yarn composed of such adhering filaments is harsh and wiry. Various substances, such as hydrocarbon oil emulsions, have been tried in the prior art to prevent this adhesion, but they have not been entirely satisfactory.

As used herein, the term "wet-spinning" refers to any process of filament formation wherein a polymer solution is injected into a liquid coagulation bath for coagulation and formation of a filament.

It is an object of the present invention to provide an improved process of wet spinning filaments so as to produce filaments which do not adhere to each other.

It is a further object to provide a novel coagulating bath which can produce filaments which do not adhere to each other.

We have now found that if the polymer solution emerging from the spinnerette is contacted with a coagulating bath containing at least about 0.005 weight percent of an organosiloxane-oxyalkylene block copolymer, the resulting solidified filaments do not tend to adhere to each other and they form soft, supple yarns. The coagulation bath can conveniently contain from about 0.005 to about 0.05 weight percent and more of an organosiloxane-oxyalkylene block copolymer. The coagulation bath preferably contains about 0.01 weight percent organosiloxane-oxyalkylene block copolymer. The organosiloxane-oxyalkylene block copolymers are especially useful as wet-spinning aids in the present invention since they are fully compatible with the coagulation baths used in industry, they do not contaminate the surfaces of the filaments and they are more effective as wet-spinning aids to reduce adhesion between spun filaments than prior art materials.

The organosiloxane-oxyalkylene copolymers useful in the compositions and processes of this invention are of the class that are known as "block" copolymers. Block copolymers are composed of at least two sections or blocks, at least one section or block composed of one type of recurring units or groups (e.g., siloxane groups as in the copolymers useful in this invention) and at least one other section or block composed of a different type of recurring units or groups (e.g., oxyalkylene groups as in the copolymers useful in this invention). Block copolymers can have linear, cyclic, branched or crosslinked structures.

The siloxane blocks in such copolymers contain at least two siloxane groups that are represented by the formula

(1) $$R_bSiO_{4-b/2}$$

wherein R is a monovalent hydrocarbon group, a halogen-substituted monovalent hydrocarbon group or a divalent hydrocarbon group and b has a value from 1 to 3. Preferably, each R contains from one to about twenty carbon atoms. The groups represented by R can be the same or different in any given siloxane group or throughout the siloxane block, and the value of b in the various siloxane groups in the siloxane block can be the same or different. The divalent hydrocarbon groups represented by R link the siloxane block to the oxyalkylene block. Each siloxane block contains at least one group represented by Formula 1 wherein at least one group represented by R is a divalent hydrocarbon group. The siloxane block has a ratio of hydrocarbon groups to silicon atoms from 1:1 to 3:1.

Illustrative of the monovalent hydrocarbon groups that are represented by the R in Formula 1 are the alkenyl groups (for example, the vinyl group and the allyl group); the cycloolkenyl groups (for example, the cyclohexenyl group); the alkyl groups (for example, the methyl, ethyl, isopropyl, octyl, dodecyl, octadecyl and eicosyl groups); the aryl groups (for example, the phenyl, naphthyl, and terphenyl groups); the aralkyl groups (for example, the benzyl and the phenylethyl groups); the alkaryl groups (such as, the styryl, tolyl and n-hexylphenyl groups), and the cycloalkyl groups (for example, the cyclohexyl group).

Illustrative of the halogen-substituted monovalent hydrocarbon groups that are represented by R in Formula 1 are the chloromethyl, trichloroethyl, perfluorovinyl, parabromobenzyl, iodophenyl, alpha-chloro-beta-phenylethyl, parachlorotolyl and bromocyclohexyl groups and the like.

Illustrative of the divalent hydrocarbon groups represented by R in Formula 1 are the alkylene groups (such as, the methylene, ethylene, propylene, butylene, 2,2-dimethyl-1,3-propylene, decylene and eicosylene groups), the arylene groups (such as the phenylene and p,p'-diphenylene groups), and the alkarylene groups (such as, the phenylethylene group). Preferably, the divalent hydrocarbon group is an alkylene group containing from two to four successive carbon atoms. Siloxane groups containing divalent groups as substituents are illustrated by groups having the formulas:

$$-CH_2CH_2SiO_{1.5},\quad -CH_2\overset{CH_3}{\underset{|}{C}}HCH_2\overset{CH_3}{\underset{|}{Si}}O_{1.0}$$

and

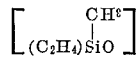
$$-CH_2CH_2\overset{CH_3}{\underset{CH_3}{|}}SiO_{0.5}-$$

These divalent hydrocarbon groups are linked to a silicon atom of the siloxane block by a silicon-to-carbon bond and to an oxygen atom of the oxyalkylene block by a carbon-to-oxygen bond.

The siloxane block can contain siloxane groups that are represented by Formula 1 wherein either the same hydrocarbon groups are attached to the silicon atoms (e.g., the dimethylsiloxy, diphenylsiloxy and diethylsiloxy groups) or different hydrocarbon groups are attached to the silicon atoms (e.g., the methylphenylsiloxy, phenylethylmethylsiloxy and ethylvinylsiloxy groups).

The siloxane block in the copolymers useful in this invention can contain one or more types of siloxane groups that are represented by Formula 1 provided that at least one group has at least one divalent hydrocarbon

siloxy groups



can be present in the siloxane block or the siloxane block can contain more than one type of siloxane group, e.g., the block can contain both ethylenemethylsiloxy groups and diphenylsiloxy groups, or the block can contain ethylenemethylsiloxy groups, diphenylsiloxy groups and diethylsiloxy groups.

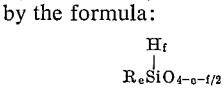
The siloxane block contained in the copolymers useful in this invention can contain trifunctional siloxane groups (e.g. monomethylsiloxane groups, $CH_3SiO_{1.5}$), difunctional siloxane groups (e.g., dimethylsiloxane groups, $(CH_3)_2SiO$—), monofunctional siloxane groups (e.g., trimethylsiloxane groups, $(CH_3)_3SiO_{0.5}$), or combinations of these types of siloxane groups having the same or different substituents. Due to the functionality of the siloxane groups, the siloxane block can be predominately linear or cyclic or branched or it can have combinations of these structures.

The siloxane block contained in the copolymers useful in this invention can contain organic end-blocking or chain terminating organic groups as well as the monofunctional siloxane chain terminating groups encompassed by Formula 1. By way of illustration, the siloxane block can contain such organic end-blocking groups as the hydroxyl group, the aryloxy groups (such as, the phenoxy group), the alkoxy groups (such as, the methoxy, ethoxy, propoxy and butoxy groups), the acyloxy groups (such as the acetoxy group), and the like.

The siloxane blocks in the copolymers useful in this invention contain at least two siloxane groups that are represented by Formula 1. Preferably, the siloxane blocks contain a total of at least five siloxane groups that are represented by Formula 1 and by Formula 1–*a* below. That part of the average molecular weight of the copolymer that is attributable to the siloxane blocks can be as high as 50,000 or greater.

A siloxane block can contain, in addition to the groups represented by Formula 1, one or more siloxane groups represented by the formula:

(1-a)



wherein R has the meaning defined in Formula 1, *e* has a value from 0 to 2, *f* has a value from 1 to 2 and *e*+*f* has a value from 1 to 3.

The oxyalkylene blocks in the copolymers employed in this invention each contain at least two oxyalkylene groups that are represented by the formula:

(2) [—R′O—]

wherein R′ is an alkylene group. Preferably, the alkylene group represented by R′ in Formula 2 contains from two to about ten carbon atoms, and most preferably from two to three carbon atoms. Water-solubility of the copolymer is enhanced when R′ contains less than three carbon atoms. It is therefore important that at least one

$$—C_2H_4O—$$

group be present in the copolymer for it to be at least partially water-soluble. Illustrative of the oxyalkylene groups that are represented by Formula 2 are the oxyethylene, oxy-1,2-propylene, oxy-1,3-propylene, oxy-2,2-dimethyl-1,3-propylene, oxy-1,10-decylene groups, and the like.

The oxyalkylene blocks in the copolymers useful in this invention can contain one or more of the various types of oxyalkylene groups represented by Formula 2. By way of illustration, the oxyalkylene blocks can contain only oxyethylene groups or only oxypropylene groups or both oxyethylene and oxypropylene groups, or other combinations of the various types of oxyalkylene groups represented by Formula 2.

The oxyalkylene blocks in the copolymers useful in this invention can contain organic end-locking or chain terminating groups. By way of illustration, the oxyalkylene blocks can contain such end-blocking groups as the hydroxy group, the aryloxy groups (such as, the phenoxy group), the alkoxy groups (such as, the methoxy, ethoxy, propoxy and butoxy groups), alkenyloxy groups (such as, the vinyloxy and the allyloxy groups). Also, a single group can serve as an end-locking group for more than one oxyalkylene block. For example, the glyceroxy group,



can serve as an end-blocking group for three oxyalkylene chains.

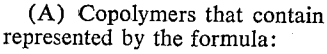
The oxyalkylene blocks in the copolymers useful in this invention each contain at least two oxyalkylene groups that are represented by Formula 2. Preferably, each block contains at least five of such groups. That part of the average molecular weight of the copolymer that is attributable to the oxyalkylene blocks can vary from 88 for $(C_2H_4O)_2$ to 50,000 or greater.

The block copolymers useful in this invention can contain siloxane blocks and oxyalkylene blocks in any relative amount. In order to possess desirable properties, the copolymer should contain from 5 parts by weight to 95 parts by weight of siloxane blocks and from 5 parts by weight to 95 parts by weight of oxyalkylene blocks per 100 parts by weight of the copolymer. Preferably, the copolymers contain 5 parts by weight to 50 parts by weight of the siloxane blocks and from 50 parts by weight to 95 parts by weight of the oxyalkylene blocks per 100 parts by weight of the copolymer.

The block copolymers useful in this invention can contain more than one of each of the blocks and the blocks can be arranged in various configurations such as, linear, cyclic or branched configurations. By way of illustration, the following classes of compounds are among the siloxane-oxyalkylene block copolymers useful in the formulations of this invention:

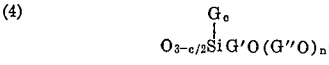
(A) Copolymers that contain at least one unit that is represented by the formula:

(3)



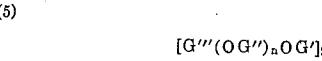
(B) Copolymers that contain at least one unit that is represented by the formula:

(4)



(C) Copolymers that contain at least one unit that is represented by the formula:

(5)



In the above Formulas 3, 4 and 5, G is a monovalent hydrocarbon radical or a halogen-substituted monovalent hydrocarbon radical, G′ is a divalent hydrocarbon radical, G″ is an alkylene radical containing at least two carbon atoms, G‴ is a hydrogen atom or a monovalent hydrocarbon radical free of aliphatic unsaturation, *n* is an integer having a value of at least two, and *c* has a value from 0 to 2 in Formulas 3 and 4 and 0 to 1 in Formula 5. In Formulas 3, 4 and 5, G can represent the same or different radicals, *n* preferably has a value from 4 to 30 and G″ can represent the same or different radicals, i.e., the groups (OG″) *n* can represent, for example, the groups: $—(OC_2H_4)_p—$, $—(OC_2H_4)_p(OC_3H_6)_q—$, $—(OC_3H_6)_p—$ or $(OC_2H_4)_p(OC_8H_{16})_q—$, where *p* and *q* are integers having a value of at least one.

The monovalent hydrocarbon radicals and halogen-substituted monovalent hydrocarbon radicals represented by G in Formulas 3, 4 and 5 can be saturated or ole-

finically unsaturated or can contain benzenoid unsaturation. Illustrative of the monovalent hydrocarbon radicals represented by G are the linear aliphatic radicals (e.g., the methyl, ethyl, decyl, octadecyl and eicosyl radicals), the cycloaliphatic radicals (e.g, the cyclohexyl and the cyclopentyl radicals), the aryl radicals (e.g., the phenyl, tolyl, xylyl, naphthyl and terphenyl radicals), the aralkyl radicals (e.g., the benzyl and betaphenylethyl radicals), the unsaturated linear aliphatic radicals (e.g., the vinyl, allyl and hexenyl radicals) and the unsaturated cycloaliphatic radicals (e.g., the cyclohexenyl radical).

Illustrative of the halogen-substituted monovalent hydrocarbon radicals represented by G are the chloromethyl, trichloroethyl, perfluorovinyl, para-bromobenzyl, iodophenyl, alpha-chloro-beta-phenylethyl, para-chlorotolyl and bromocyclohexyl groups and the like.

Preferably, the G and G' groups [included in the definition of R in Formulas 1 and 1–*a* above] contain from one to about twenty carbon atoms and the G'' groups [included in the definition of R in Formula 2 above] contain from two to about ten carbon atoms. When the G''' group is a monovalent hydrocarbon radical free of aliphatic unsaturation, it preferably contains from one to about twelve carbon atoms.

Illustrative of the divalent hydrocarbon radicals represented by G' in Formulas 3, 4 and 5 are the alkylene radicals (e.g., the methylene, ethylene, 1,3-propylene, 1,4-butylene, 1,12-dodecylene and 1,20-eicosylene radicals), the arylene radicals (e.g., the phenylene radical) and the alkarylene radicals (e.g. the phenylethylene radicals). In Formulas 3, 4 and 5, G' is preferably an alkylene radical containing at least two carbon atoms.

Illustrative of the alkylene radicals containing at least two carbon atoms represented by G'' in Formulas 3, 4 and 5 are the ethylene, 1,2-propylene, 1,3-propylene, 1,6-hexylene, 2-ethylhexylene-1,6 and 1,12-dodecylene radicals.

Illustrative of the radicals represented in G''' in Formulas 3, 4 and 5 are the saturated linear or branched chain aliphatic hydrocarbon radicals (e.g., the methyl, ethyl, propyl, n-butyl, tert.-butyl and decyl radicals), the saturated cycloaliphatic hydrocarbon radicals (e.g., the cyclopentyl and cyclohexyl radical) the aryl hydrocarbon radicals (e.g., the phenyl, tolyl, naphthyl and xylyl radicals), and the aralkyl hydrocarbon radicals (e.g., the benzyl and betaphenylethyl radicals).

The following are representative of the hydrolytically stable siloxane-oxyalkylene block copolymers useful in this invention. In the formulas, Me represents methyl (CH_3), Et represents ethyl (CH_3CH_2), ϕ represents phenyl (C_6H_5), Bu represents n-butyl ($CH_3CH_2CH_2CH_2$) and x is an integer. Where the formula represents a unit of a polymer, it is understood that the polymer is terminated by end-blocking groups of the type described hereinabove.

(a) $(Me_3SiO)_2SiCH_2CH_2O(C_3H_6O)_{11}Bu$

(b) $Bu(OC_3H_6)_{11}OCH_2CH_2SiO(Me_2SiO)_{12}SiCH_2CH_2O(C_3H_6O)_{11}Bu$

(c) $Me_3SiO(Me_2SiO)_9(EtSiO)_3SiMe_3$ with $CH_2CH_2O(C_3H_6O)_{11}Bu$

(d) $Me_3SiO(EtSiO)_5(EtSiHO)_6SiMe_3$ with $CH_2CH_2O(C_3H_6O)_{14}(C_2H_4O)_{18}Bu$

(e) $[MeOCH_2CH_2OCH_2CH_2SiMeO]_4$ (a cyclic tetramer)

(f) $[\phi CH_2CH_2OCH_2CH_2SiO_{1.5}]_x$

(g) $Me_3SiOSiMe(OSiMe_3)CH_2CH_2O(C_2H_4O)_4Me$

(h) $[BuO(C_2H_4O)_7(C_3H_6O)_7CH_2CHCH_2SiO(SiO)_5Si]_2O$

(i) $(Me_3SiO)_2SiCH_2CH_2O(C_3H_6O)_{14}(CH_2)_8OCH_2CH_2Si(OSiMe_3)_2$

(j) $[-Si(OSiMe_3)CH_2CH_2O(CH_2CH_2O)_{19}(CH_2)_8OCH_2CH_2SiO(Me_3SiO)-]_x$

(k) $[-SiCH_2CH_2O(CH_2CH_2O)_{19}(CH_2)_8OCH_2CH_2-SiO(SiMe_3)-(Me-Si(OSiMe_3)-Me)_4]_x$

(l) $Me_3SiO(SiO)_3(Me_2SiO)_{10}SiMe_3$ with $CH_2CH_2O(C_3H_6O)_{11}Bu$ and $CH_2CH_2O(C_3H_6O)_{11}Bu$

(m) $[-SiO(CH_2CH_2O(CH_2CH_2O)_{17}Me)(CH_2CH_2O(CH_2CH_2O)_{17}Me)]_x$

(n) $Me_3Si(O-Si(Me)_2)_8OSiMe_2CH_2CH_2(OC_2H_4)_{10}OCH_2$

$Me_3Si(OSi(Me)_2)_8OSiMe_2-CH_2CH_2-(OC_2H_4)_{10}-OCH_2-CH$

$Me_3Si(O-Si(Me)_2)_8OSiMe_2CH_2CH_2(OC_2H_4)_{10}O$

(o) $BuO(C_3H_6O)_{12}CH_2-CH(Me)-CH_2$ with $BuO(C_3H_6O)_{12}CH_2CHCH_2SiMe_2O(-SiMe_2O-)_4SiMe_2$ and $BuO(C_3H_6O)_{12}CH_2CHCH_2Si(OSiMe_2)_4$

The siloxane-oxyalkylene block copolymers useful in this invention can be prepared by several convenient methods. For example, the copolymers useful in this invention can be produced by a process that involves forming a mixture of a siloxane polymer containing a silicon-bonded, halogen-substituted monovalent hydrocarbon group and an alkali metal salt of an oxyalkylene polymer and heating the mixture to a temperature sufficiently elevated to cause the siloxane polymer and the salt to react to produce the copolymer. This process is referred to herein as the "metathesis process" and it involves a metathesis reaction that can be illustrated by the following equation:

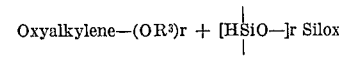
(6) $Siloxane-(OSiR_2X)_r + (MO)_r-Oxyalkylene \longrightarrow Siloxane-(OSiR^2O)_r-Oxyalkylene + rMX$

wherein R^2 is a divalent hydrocarbon group, r is an in-

teger that has a value of at least 1 and preferably 1 to about 4, X is a halogen atom, M is an alkali metal, Siloxane denotes a siloxane block and Oxyalkylene denotes an oxyalkylene block.

The copolymers useful in this invention can also be produced by another process (termed the "addition process") that involves forming a mixture of a siloxane polymer containing a hydrogen-siloxy group (i.e., a

an oxyalkylene polymer containing an alkenyloxy end-blocking or chain terminating group and a platinum catalyst and heating the mixture to a temperature sufficiently elevated to cause the siloxane polymer and the oxyalkylene polymer to react to produce the copolymer. The latter-mentioned reaction is an addition reaction that can be illustrated by the following equation:



(7) Oxyalkylene—$(OR^3)r$ + [HSiO—]r Siloxane

Oxyalkylene—[OR^4SiO—]r Siloxane

wherein oxyalkylene, siloxane and *r* have the meaning defined for Equation 6, OR^3 is an alkenyloxy group (such as, the vinyloxy and the allyloxy groups) and R^4 is an alkylene group containing at least two successive carbon atoms. The addition process is applicable to the production of those copolymers of this invention containing a siloxane block that is linked to an oxyalkylene block by an alkylene group that has at least two successive carbon atoms (e.g., an ethylene, 1,2-propylene or 1,2-butylene group and the like).

When the polysiloxane-oxyalkylene block copolymer contains silicon-bonded hydrogen atoms, i.e., contains units represented by Formula 1–*a* described above, the addition process is preferable. If the metathesis process is used, many of the silicon-bonded hydrogen atoms will react with the alkali metal ions present in the reaction mixture.

When the copolymers useful in this invention contain olefinically unsaturated groups attached to silicon (for example, when R in Formula 1 or 1–*a* above is alkenyl or cycloalkenyl, such as vinyl or cyclohexenyl) it is preferable to prepare these copolymers by addition of the alkenyloxy-end-blocked oxyalkylene polymer to a monomeric, hydrolyzable silane containing silicon-bonded hydrogen, followed by cohydrolysis or co-condensation with other hydrolyzable silanes containing silicon-bonded hydrogen and silicon-bonded olefinically unsaturated hydrocarbon groups using conventional techniques known to those versed in the art. For example, reaction of

$$CH_2{=}CHCH_2(OC_2H_4)_6OCH_3$$

with CH_3SiHCl_2 in the presence of a platinum catalyst folowed by cohydrolysis of the product with

$$CH_2{=}CHSi(CH_3)Cl_2$$

CH_3SiHCl_2, and $(CH_3)_3SiCl$ gives a copolymer useful in this invention containing units having the formulas

$$CH_3O(C_2H_4O)_6CH_2CH_2CH_2Si(CH_3)O$$

$CH_2{=}CHSi(CH_3)O$ and CH_3SiHO, endblocked with

$$(CH_3)_3SiO$$

groups.

Organosiloxane-oxyalkylene block copolymers which are especially useful in the present invention have the following formulas:

(p) $Me_3Si(OSiMe_2)_6[OMeSiCH_2CH_2CH_2O(C_2H_4O)_8Me]_7OSiMe_3$

(q) $Me_3Si(OSiMe_2)_{19}[OMeSiCH_2CH_2CH_2O(C_2H_4O)_{19}(C_3H_6O)_{14}Bu]_3OSiMe_3$

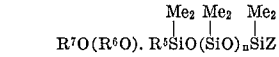
(r) $Me_3Si(OSiMe_2)_7[OMeSiCH_2CH_2CH_2O(C_2H_4O)_{15}Me]_3OSiMe_3$

(s) $Me_3SiO(Me_2SiO)_{21}[Bu(OC_2H_4)_{18}(OC_3H_6)_{14}OC_3H_6SiMeO]_{3.5}SiMe_3$

(t) $Me_3SiO(Me_2SiO)_{8.5}[Me(OC_2H_4)_{16}OC_3H_6SiMeO]_{3.5}SiMe_3$

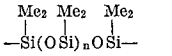
(u) $Me_3SiO(Me_2SiO)_{5.1}[Me(OC_2H_4)_{7.2}OC_3H_6SiMeO]_{7.5}SiMe_3$

Another species of block copolymer useful in the present invention has the formula:

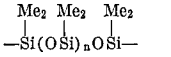


$R^7O(R^6O)_y$. $R^5SiO(SiO)_nSiZ$

in which the



group represents 5 to 60% by weight of the total weight of the copolymer, the total number of $(R^6O)_y$ groups constitutes at least 25% by weight of the copolymer and in which formula the sum of the weights of



and $—(R^6O)_y$ is not less than 50% of the copolymer, R^7 is a hydrogen substituent, a monovalent hydrocarbon radical, a monovalent hydrocarbonoxy radical, a monovalent acyl radical of carboxylic acids, a monovalent tris-hydrocarbyl silyl group or a monovalent hydrocarbon carbonyl radical, R^6 is an alkylene radical having 2, 3 or 4 carbon atoms, *y* is a whole number between 4 and 2000 inclusive, R^5 is a divalent non-aromatic hydrocarbon radical, a divalent non-aromatic hydroxy hydrocarbon radical, a divalent non-aromatic acyl radical derived from monocarboxylic acids or a divalent non-aromatic hydroxy ether radical, R^5 being bound to the silicon by a silicon-carbon bond, *n* is equal to 0 or a positive whole number and Z is a monovalent hydrocarbon radical, a monovalent hydrocarbonoxy radical, a $—R^5(OR^6)_yOR^7$ radical, in which R^5, R^6, *y* and R^7 are as defined above, or a radical of the formula $—ASiB_3$ in which A is a divalent hydrocarbon radical and B is a monovalent hydrocarbon radical or a dihydrocarbylsiloxy radical.

Polymeric filaments produced by the process of the present invention can be obtained from any polymer or polymer derivative that can be coagulated in filament form in a liquid coagulation bath. Such polymeric filament raw materials include acrylic polymers, such as polyacrylonitrile and copolymers of acrylonitrile with vinyl chloride, vinylidene chloride or vinyl acetate, for example, wherein the copolymer contains at least 85 weight percent acrylonitrile units; modacrylic polymers, such as copolymers of acrylonitrile with vinyl chloride, vinylidene chloride or vinyl acetate, for example, wherein the copolymer contains at least 35 weight percent acrylonitrile units and less than 85 weight percent acrylonitrile units; polyvinyl alcohols, such as $[—CH_2—CHOH—CH_2CHOH]_n$; nitrile polymers, such as vinylidene cyanide and copolymers of vinylidene cyanide and vinyl acetate, for example, wherein the copolymer contains at least 85 weight percent vinylidene cyanide; polyurethanes, such as

$$[—(CH_2)_4OOCNH(CH_2)_6NHCOO—]_n$$

and the polymeric reaction product between an adipic acid-ethylene glycol copolymer and 4,4′-diphenylmethane diisocyanate and copolymers of polyurethanes with other organic polymers, such as vinyl chloride, vinylidene chloride or vinyl acetate, for example, wherein the copolymer contains at least 85 weight percent polyurethane units; and the like.

The polymeric filament raw materials are generally introduced to the coagulating bath as a spinning solution in some convenient solvent. Typical solvents for the raw material spinning solution are acetonitrile, nitromethane, nitroethane, dimethylformamide, dimethylacetamide, ethylene carbonate, acetone, gamma-butyrolactone, ethylene carbamate, N-methyl-2-pyrolidone, and the like. The spinning solution solvent is generally an organic liquid since the polymeric filament raw materials are insoluble

in water. The spinning solution can also contain a minor amount of water, if desired. It is preferable that the spinning solution solvent be water soluble for convenience in subsequent processing.

The coagulation bath contains water or an equivalent non-solvent for the polymeric filament raw material. The coagulation bath is also miscible with the spinning solution solvent. It is preferred to have the coagulation bath contain a minor amount of an organic liquid solvent of the same composition or which has similar solvent properties as the spinning solution solvent. This enables improved control to be obtained over the rate of solvent removal from the spinning solution and thus gives improved control over coagulated filament quality. For example, when the spinning solution solvent is primarily acetonitrile, the coagulating bath can contain up to about 40 weight percent acetonitrile but preferably from about 5 to about 20 weight percent acetonitrile based on total weight of the coagulating bath.

During coagulation of the polymeric filament raw material to form solid polymeric filaments, several processes may proceed simultaneously: osmosis of the spinning solution solvent, diffusion of any solutes present in the polymer solution and the coagulating bath, chemical reaction between any diffusing substances and the polymer, salting out effects and electrolytic effects. The exact mechanism of coagulation, in a given filament-forming process will depend upon the specific polymer solution-coagulating bath composition combination being used. In the case of wet-spinning polyacrylics, for example, the coagulation mechanism generally involves diffusion of the spinning solvent from the polymer spinning solution into the surrounding coagulating bath. This lowers the solubility of the polymer and forms the coagulated solid filament. The novel coagulating baths of the present invention include all of the useful baths used by industry for wet-spinning filaments, such novel baths containing the above critical amounts of organosiloxane-oxyalkylene block copolymers. When the novel coagulating baths and improved wet-spinning processes of the present invention are employed, the overall prior art wet-spinning techniques, such as temperatures and processing rates, are also employed.

The invention is described in further detail with respect to the following example.

Example

A 23 weight percent total solids solution of a modacrylic resin (containing 70 weight percent acrylonitrile and 30 weight percent vinyl chloride in the resin) in a solvent mixture consisting of 98 weight percent acetonitrile and 2 weight percent water was extruded through a spinnerette having 30 holes each 0.13 mm. in diameter into a 65° C. coagulating both consisting of a mixture of 90 weight percent water and 10 weight percent acetonitrile. The polymer solution was coagulated into solid filaments which were removed from the coagulating bath, washed and dried. The resulting filaments formed a harsh, cemented fiber bundle of less than 30 filament entities.

The run was repeated with a coagulating bath of the above composition also containing 0.01 weight percent of an organosiloxane-oxyalkylene block copolymer having the formula:

$$Me_3SiO(Me_2SiO)_{21}[Bu(OC_2H_4)_{18}(OC_3H_6)_{14}OC_3H_6SiMeO]_{3.5}SiMe_3$$

A soft, non-cemented filament bundle of 30 filament entities was obtained.

What is claimed is:

1. In a process for the production of polymeric filaments by wet spinning which comprises extruding a polymeric filament raw material spinning solution through a spinnerette into a coagulating bath capable of coagulating the polymeric filament raw material into a solid filament form which can then be removed from the coagulating bath for subsequent processing, the improvement which comprises contacting the polymeric filament raw material spinning solution extruded from a spinnerette with a coagulating solution containing at least 0.005 weight percent of an organosiloxane-oxyalkylene block copolymer comprising (a) at least one siloxane block containing at least two siloxane units represented by the formula:

$$R_bSiO_{4-b/2}$$

wherein R contains from one to about twenty carbon atoms and is selected from the class consisting of monovalent hydrocarbon groups, halogen-substituted monovalent hydrocarbon groups and divalent hydrocarbon groups and *b* has a value from 1 to 3 inclusive, said siloxane block containing at least one of said siloxane units wherein at least one R group is a divalent hydrocarbon group, and (b) at least one oxyalkylene block containing at least two oxyalkylene groups represented by the formula —R'O—, wherein R' is an alkylene group containing from two to about ten carbon atoms, said siloxane and oxyalkylene blocks being interconnected by said divalent hydrocarbon group.

2. A process for the production of polymeric filaments as claimed in claim **1** wherein the coagulating bath contains from about 0.005 to about 0.05 weight percent of an organosiloxane-oxyalkylene block copolymer.

3. A process for the production of polymeric filaments as claimed in claim **1** wherein the coagulating bath contains about 0.01 weight percent of an organosiloxane-oxyalkylene block copolymer.

4. A process for the production of polymeric filaments as claimed in claim **1** wherein the organosiloxane-oxyalkylene block copolymer has the formula:

$$Me_3SiO(Me_2SiO)_{21}[Bu(OC_2H_4)_{18}(OC_3H_6)_{14}OC_3H_6SiMeO]_{3.5}SiMe_3$$

5. An improved coagulation bath for wet spinning of polymeric filaments which comprises (1) a major amount of a liquid which is not a solvent for the raw materials from which the polymeric filaments are produced, (2) a minor amount of an organic liquid which is a solvent for the raw materials from which the polymeric filaments are produced and (3) at least 0.005 weight percent of an organosiloxane-oxyalkylene block copolymer comprising (a) at least one siloxane block containing at least two siloxane units represented by the formula:

$$R_bSiO_{4-b/2}$$

wherein R contains from one to about twenty carbon atoms and is selected from the class consisting of monovalent hydrocarbon groups, halogen-substituted monovalent hydrocarbon groups and divalent hydrocarbon groups and *b* has a value from 1 to 3 inclusive, said siloxane block containing at least one of said siloxane units wherein at least one R group is a divalent hydrocarbon group, and (*b*) at least one oxyalkylene block containing at least two oxyalkylene groups represented by the formula —R'O—, wherein R' is an alkylene group containing from two to about ten carbon atoms, said siloxane and oxyalkylene blocks being interconnected by said divalent hydrocarbon groups.

6. An improved coagulation bath as claimed in claim **5** wherein the organosiloxane-oxyalkylene block copolymer is present in an amount from about 0.005 to about 0.05 weight percent.

7. An improved coagulation bath as claimed in claim **5** wherein the organosiloxane-oxyalkylene block copolymer is present in an amount of about 0.01 weight percent.

8. An improved coagulation bath as claimed in claim

5 wherein the organosiloxane-oxyalkylene block copolymer has the formula:

$$Me_3SiO(Me_2SiO)_{21}[Bu(OC_2H_4)_{18}(OC_3H_6)_{14}OC_3H_6SiMeO]_{3.5}SiMe_3$$

9. The improved coagulation bath as claimed in claim 5 wherein water is the liquid which is not a solvent for the raw materials from which the polymeric filaments are produced and wherein the organic liquid which is a solvent for the raw materials from which the polymeric filaments are produced is a member selected from the group consisting of acetonitrile, nitromethane, nitroethane, dimethylformamide, dimethylacetamide, ethylene carbonate, acetone, gammabutyrolactone, ethylene carbamate and N-methyl-2-pyrolidone.

10. The process of claim 1 wherein the polymeric filament raw material is an acrylonitrile polymer.

11. The process of claim 1 wherein the polymeric filament raw material is a polyurethane.

12. The process of claim 1 wherein the polymeric filament raw material is a polyvinyl alcohol.

13. The process of claim 1 wherein the polymeric filament raw material is a polymeric reaction product of an adipic acid-ethylene glycol copolymer and 4,4'-diphenylmethane diisocyanate.

References Cited

UNITED STATES PATENTS

1,028,748	6/1912	Lederer.	
2,834,748	5/1958	Bailey et al.	260—46.5 XR
3,109,697	11/1963	Cipriani et al.	264—200
3,140,198	7/1964	Dawson et al.	252—8.9

FOREIGN PATENTS

802,467	10/1958	Great Britain.

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