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3,793,277

SOLUTION AND METHOD OF DELUSTERING ACRYLIC FIBERS WITH PARTICULATE METAL SALT DISPERSANT OF COPOLYMER OF 1-OLEFIN AND MALEIC ANHYDRIDE COMPOUND AS AID

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ABSTRACT OF THE DISCLOSURE

Delustering polyacrylonitrile fibers by dispersing a particulate delustrant in a mixture of a solvent comprising a lower alkyl nitrile having from 2 to 4 carbon atoms and a metal salt of a copolymer of a maleic anhydride and a 1-olefin, and incorporating the delustrant dispersion into polyacrylonitrile to form a spinning solution.

The present invention relates to a method for producing delustered high acrylonitrile polymer fibers. More particularly, it relates to a method for the uniform dispersion of a finely divided particulate delustrant throughout solutions used in spinning fibers from high acrylonitrile polymers, with minimal aggregation, i.e., clumping, flocculation, agglomeration, and the like, of the delustrant particles.

It is well known that polyacrylonitrile and copolymers of acrylonitrile with at least one other ethylenically unsaturated compound are excellent fiber-forming polymers. The polyacrylonitrile and polymers of more than 85 percent acrylonitrile and up to about 15 percent of other ethylenically unsaturated compounds produce fibers with superior tensile properties, desirable elongation and excellent stability under a wide range of physical and chemical conditions. However, these fibers, as spun, have a high sheen or luster which is a serious disadvantage for many fiber end uses.

It is necessary to produce delustered fibers for many textile end uses. Many of the synthetic organic polymeric fibers are characterized by a high surface sheen when spun in a conventional manner. This surface sheen or luster may be eliminated or diminished by the addition of melt additives, surface finishes and the like to modify the light reflectance characteristics of the surface of the fiber.

The more luxurious natural fibers, particularly wool, exhibit a very low sheen or luster. When a synthetic fiber is to be used for such end uses as dresses, carpets, men's suits, and the like, which are substantial outlets for wool yarns, it is necessary to modify the surface characteristics of the fibers to reduce their sheen to produce a fiber which resembles the natural fibers in appearance. A product having a glossy, shiny surface will most often be considered inferior in the marketplace when compared to the dull appearing wool product. Acrylic fibers are often utilized as wool substitutes and, therefore, must be compatible with wool in appearance.

Generally, it is a relatively simple operation to incorporate a finely divided delustrant into a fiber-forming synthetic organic polymer spinning solution. Normally, with an acrylonitrile polymer spinning solution, one of the components of the spinning solution acts as a carrier for the particulate delustrant. The delustrant is added and thereafter mechanically dispersed throughout the spinning solution, preparatory to extrusion.

There are certain circumstances when it becomes impracticable to incorporate delustrant into acrylonitrile fibers in the conventional manner. This is especially true

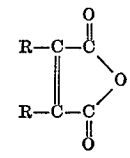
for fiber-forming acrylonitrile polymer solution wherein during spinning the spinning solution is maintained under superatmospheric pressure and at a temperature above the atmospheric boiling point of the solvent. In such a system the delustrant normally must be dispersed in a fluid medium before injection into the spinning system to avoid clustering or flocculation of the particulate delustrant. The present process is particularly applicable to acrylonitrile polymers in low boiling solvents, such as acetonitrile or acetonitrile and up to about 40 weight percent water, the solutions of which solidify at temperatures below the atmospheric boiling point and/or upon the release of the imposed superatmospheric pressure.

It is an object of the present invention to provide spinning solutions of polymers containing at least 85 percent acrylonitrile having dispersible delustrants substantially uniformly distributed throughout. It is another object of the present invention to provide a method for stable spinning of delustered acrylic fibers wherein during spinning the spinning solution is maintained under superatmospheric pressure and at a temperature above the atmospheric boiling point of the solvent. These and other objects will be apparent to those skilled in the art from the description of the invention which follows.

These objects are accomplished according to the present invention by dispersing a particulate delustrant such as a colored pigment or pigmentary TiO_2, preferably of a particle size of less than about 10 microns, most preferably less than 5 microns, in a mixture of a metal salt of a copolymer of a maleic anhydride with a 1-olefin and an acrylonitrile solvent consisting essentially of a lower alkyl nitrile having from 2 to 4 carbon atoms, preferably acetonitrile which is mixed with up to about 40 percent water, by weight, based on the weight of acetonitrile. The mixture, prior to addition of the delustrant, comprises from about 1 percent to 10 percent by weight maleic anhydride copolymer in the lower alkyl nitrile solvent for high acrylonitrile polymers. The dispersion of the delustrant or pigment in the solution comprises from about 10 to 45 percent, preferably from about 15 to 30 percent, by weight, particulate delustrant; from about 0.05 to 9 percent, preferably from about 1 to 5 percent, by weight, maleic anhydride copolymer, and from about 46 to 89 percent, preferably from about 60 to 80 percent, by weight, lower alkyl nitrile solvent.

The polymeric dispersing agents with which this invention is concerned are 1-olefin copolymers with maleic anhydride or other unsaturated anhydride, which are in the form of a metal salt, preferably an alkali metal salt.

Maleic anhydride will polymerize with 1-olefins to produce polymers for use as the dispersant in the process of this invention. Similar unsaturated anhydrides can also be used. These can be shown by the formula:



where each R is individually selected from the group consisting of hydrogen, methyl and ethyl. Examples include maleic anhydride, monomethylmaleic anhydride, diethylmaleic anhydride, and methylethylmaleic anhydride. Mixtures of these materials can also be used.

The olefins should contain 4 to 16, preferably 6 to 10, carbon atoms. Examples include 1-butene, isobutylene, 1-pentene, 2-methyl-1-butene, 3-methyl-1-butene, 1-hexene, 1-heptene, 1-octene, 2,4,4-trimethyl-1-pentene (diisobutylene), 1-nonene, 1 - tetradecene, and 1-hexa-

decene. Mixtures of olefins, such as diisobutylene, can also be used.

Examples of these copolymers include those of maleic anhydride/1-butene, dimethylmaleic anhydride/3-methyl-1-butene, ethylmaleic anhydride/1-octene, etc.

Copolymers of 1-olefins and maleic anhydride have been made for many years. They can be made by copolymerizing the anhydride, preferably in solution in an organic diluent such as benzene, with the olefin in the presence of a peroxide catalyst. Elevated temperatures and superatmospheric pressures are usually employed. The monomers copolymerize in substantially equimolar proportions.

The sodium salt of a copolymer of diisobutylene and maleic anhydride is especially suitable as the dispersant in the process of this invention. Such a product is that sold under the trademark Tamol 731 by Rohm and Haas Company. Another suitable product is sold under the trademark Trenamine W–25 by Alco Oil and Chemical Corporation.

The delustrant mixture may be ground or milled with the dispersant in a conventional manner to form a master batch dispersion. The dispersion is then mixed with the preformed polyacrylonitrile spinning solution.

Alternatively, the dispersion may be incorporated into the spinning solution by first mixing the dispersion with the acrylonitrile polymer solvent, then adding acrylonitrile polymer powder. After incorporating the delustrant dispersion into the spinning solution, the mixture is stabilized against flocculation, by mixing in a suitable container, such as by tumbling in a stainless steel bomb for from about 1 to 5 hours. The mixture is preferably simultaneously heated while mixing. The dispersion may also be mixed with the acrylonitrile polymer prior to solvation of the polymer.

The present invention requires that a solution be utilized for dispersing the pigment prior to addition to the acrylonitrile polymeric spinning solution. Although acetonitrile is the preferred solvent, any lower alkyl nitrile having from 2 to 4 carbon atoms may be used alone, or mixed with up to about 40 weight percent water. When solutions of acetonitrile utilizing such dispersants as Tamol 850 (Tamol 850 is a trademark of Rohm and Haas Company for an anionic surfactant which is the sodium salt of a polymeric carboxylic acid); Tergitol 4, 7 (Tergitol 4 and Tergitol 7 are trademarks of Union Carbide Corporation for anionic surfactants which are, respectively, sodium tetradecyl sulfate and sodium hecadecyl sulfate); hydroxyethyl cellulose; Ethoguad; Ethomeen; Ethoduomeen; Ethofat or Ethomid (Ethoquad, Ethomeen, Ethoduomeen, Ethofat and Ethomid are trademarks of Armour Industrial Chemical Company for surfactants which are, respectively, polyethoxylated quaternary ammonium chlorides derived from long chain amines, polyethoxylated aliphatic amines with alkyl groups ranging from C–8 to C–18, polyethyoxylated high molecular weight aliphatic diamines, polyethyoxylated fatty acids and polyethoxylated high molecular weight amides) are used to disperse TiO_2, flocculation or clustering results, particularly when subsequently combined with the polyacrylonitrile spinning solution which utilizes the noted low boiling solvent system.

When flocculation occurs spinning is difficult, if not impossible. Even when spinning is possible, it is characteristically unstable with a large number of broken filaments. Such a process is both economically and practically unfeasible.

As referred to herein, acrylonitrile polymers are those containing at least 85 percent acrylonitrile polymers and preferably those containing at least 90 percent acrylonitrile by weight. These polymers can be acrylonitrile homopolymers, as well as copolymers, terpolymers, multipolymers and the like wherein up to about 15 per cent, preferably up to 10 percent, of the polymer is another ethylenically unsaturated compound copolymerizable with the acrylonitrile. Such materials can be monomers of polymers which are copolymerizable with acrylonitrile and added to modify and/or enhance certain characteristics of the acrylic polymer. Often, the material copolymerizable with the acrylonitrile contains a chemical group which increases the acid or dyeability of the resulting polymer. Such dye enhancing compounds normally contain a sulfur or phosphorous group in the ethylenically unsaturated chemical entity copolymerizable with the acrylonitrile. Typically, such sulfur- or phosphorous-containing compounds are added in an amount of about 0.1 up to about 5 percent by weight of the total polymer composition while the other modifying substance, if any, is added in an amount of up to about 14.9 percent. Typical ethylenically unsaturated monomers copolymerizable with acrylonitrile are methyl acrylate, vinyl acetate, vinylidene chloride, methyl methacrylate, methallyl alcohol, vinylidene cyanide, styrene sulfonic acid materials, sodium methallyl sulfonate, mixtures and partial polymers thereof and the like as are well known to those skilled in the art. The polymers are polymerized by conventional methods such as solution or suspension polymerizations, as well known in the art.

The degree to which the polymer is polymerized is dependent on the end use for which the polymer is intended. Thus, for spinning acrylic fibers, the polymer is preferably polymerized to an intrinsic viscosity of about 0.9 to 2.0 or more, and more preferably about 1.2 to 1.8 (I.V. in a 0.1% solution of the polymer in N,N-dimethylformamide at 25 degrees centigrade). Of course, higher I.V.'s can be used but they result in higher viscosities for given solvent concentrations. For films, molded products, extruded non-fiber products and the like, different I.V.'s may be more desirable.

In the solution spinning of fibers, it is preferable to use a high solids concentration in the spinning solution. With the preferred solvent system, such high solid concentrations are readily obtained using the acrylic polymers having I.V.'s in the normal range used for acrylic fiber spinning, that is, about 1.2 to 1.8. In particular, solutions of a solids content of about 30 to 70 percent by weight are obtained. The more preferred spinning solutions are obtained in the solid range of about 30 to 50 percent with polymers having I.V.'s of about 1.2 to 1.8 or more. With lower I.V. polymers, such as about 0.9 to 1.2, higher solids contents up to about 70 percent or more can be used.

The spinning solutions are formed by mixing the desired solid amount of acrylonitrile polymer with acetonitrile by itself or with water in an amount up to about 50 weight percent of the total solvent portion. While a water addition need not be used, it has been found that the addition of water, particularly in the range of about 18 to 27 percent by weight of the acetonitrile solvent portion, lowers the gelation point of the resulting solution, thereby enabling greater flexibility and control of spinning, molding or extruding temperatures.

The acrylic polymer and acetonitrile solvent portion are mixed and cooled to a low temperature, e.g., 0 to —7 degrees centigrade. Mixing is continued, usually for 1 to 7 hours wherein the polymer passes from a solid into a slurry state. The slurry is then heated under superatmospheric pressure to a temperature above the atmospheric boiling point of the solvent and below the polymer degradation temperature (i.e., 80 to 160 degrees centigrade, preferably 90 to 140 degrees centigrade) and held at that temperature for about 1 to 20 hours during which time the slurry passes into a liquid state. Having reached the liquid state, the temperature can then be lowered to about 80 to 85 degrees centigrade without gelation, if pressure is maintained. The gel temperature on cooling is normally above or near the boiling point of the acetonitrile under process pressure depending on the amount of water

present, the polymer I.V., the acrylonitrile content, the solids content and the like.

The superatmospheric pressure utilized to form the solution is preferably at least equal to that required to maintain the acetonitrile solvent portion in substantially the liquid phase. For example, at 130 degrees centigrade and 34 percent solids, the vapor pressure of the dope is approximately 58 p.s.i.g. At 90 degrees centigrade, the vapor pressure is only 20 p.s.i.g.; however, higher pressures such as 100 to 300 p.s.i.g. can conveniently be used if desired.

The invention will be more fully described by reference to the following examples which illustrate certain preferred embodiments of the present invention. Unless otherwise indicated, all temperatures are in degrees centigrade and all parts are by weight.

EXAMPLE I

An acrylonitrile copolymer comprising about 94.5 percent acrylonitrile, about 5 percent methylacrylate and about 0.5 percent sodium methallyl sulfonate, polymerized to an intrinsic viscosity of about 1.4 and a molecular weight of about 110,000 was solvated with acetonitrile by placing 36 pounds of the acrylonitrile copolymer into a pressure vessel together with 51.2 pounds of acetonitrile and 12.8 pounds of water. The resulting mixture comprised 36 percent acrylonitrile copolymer solids, 12.8 percent water and 51.2 percent acetonitrile, by weight (the acetonitrile/water were in a proportion of about 80/20, by weight).

The pressure vessel was sealed and subsequently slowly mixed for eight hours at room temperature, then the temperature was raised slowly to 110 degrees centigrade, at which point the material in the vessel changed from a slurry to a gel-like phase into a homogeneous fluid solution (dope). The mixture was then mixed for about 18 hours more at 110 degrees centigrade while maintaining a pressure of about 50 p.s.i.g., creating a dope viscosity of about 100 poises, at the noted temperature.

A solution comprising about 4 percent, by weight, of a dispersant which is a sodium salt of a copolymer of diisobutylene and maleic anhydride (Tamol 731) and about 96 percent, by weight, 80/20 acetonitrile/water was prepared in a conventional manner. Anatase TiO_2 was added to the solution in an amount such that the mixture contained about 20 percent by weight TiO_2, about 3 percent by weight dispersant and about 77 percent by weight 80/20 acetonitrile/water. The TiO_2 pigment was dispersed throughout the solution by grinding in a ball mill. After ball milling for about 3 hours, sufficient TiO_2 dispersion (wherein the TiO_2 particle size was less than about 2 microns) was incorporated into the dope to give 0.25 percent TiO_2 by weight based on acrylonitrile polymer by adding the dispersion and spinning dope to a stainless steel bomb. The dispersion was then tumbled for about 3 hours at 110–135 degrees centigrade.

The spinning dope prepared by the above procedure was passed to a pressurized dry spinning system. The spinning dope was maintained at a temperature of about 130 degrees centigrade and a pressure of 50 p.s.i.g. Filaments were spun from the solution using a spinneret having 150-micron jet openings of round configuration. The filaments were dry spun at 100 meters per minute into a column maintained at a temperature of from about 40 to 60 degrees centigrade. The resulting filaments had a low sheen (i.e., were delustered) and had substantially round, serrated cross sections. The as-spun filaments were subsequently after-drawn at a draw ratio of about 2:1.

EXAMPLE II

The method of Example I was repeated, except that the TiO_2 dispersion in the dispersant—acetonitrile/water solution—was added to the acetonitrile/water spinning solvent together with the acrylonitrile copolymer, prior to solvation of the acrylonitrile copolymer with the acetonitrile/water spinning solvent. The mixture was then tumbled in a stainless steel bomb for about 3 hours at 110 to 135 degrees centigrade. The dope was then spun as in Example I. The spun filaments were delustered, as in Example I.

EXAMPLE III

The method of Example I was repeated, except that the solution initially prepared contained about 2.5 percent by weight dispersant dissolved in 80/20 acetonitrile/water. The final TiO_2 dispersion contained about 20 percent by weight TiO_2, about 2 percent by weight dispersant, and about 78 percent by weight 80/20 acetonitrile/water. This dispersion was added to the acrylonitrile polymer spinning solution as in Example II and a fiber spun which contained about 0.2 percent by weight, based on the weight of acrylonitrile copolymer, of TiO_2. The spun filaments were delustered, as in Example I.

EXAMPLE IV

The method of Example I was repeated, except that the initial solution prepared contained about 1.5 percent by weight dispersant in 80/20 acetonitrile/water. TiO_2 was added to this solution such that a mixture containing about 1 percent by weight Tamol 731 and 79 percent by weight 80/20 acetonitrile/water and 20 percent by weight TiO_2 resulted. The TiO_2 was dispersed throughout the solution, as in Example I, and added to the acrylonitrile polymeric spinning solution, as in Example I. Filaments were spun which contained about 0.2 percent by weight, based on the weight of acrylonitrile copolymer, of TiO_2. The spun filaments were delustered as in Example I.

EXAMPLE V

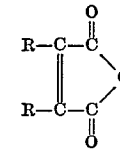
The method of Example I was repeated, except that other dispersants were used in varying percentages, as shown in Table 1 below. The dispersions were all unstable as evidenced by flocculation, and were unsuitable for use as a fiber delustrant dispersion.

TABLE 1

Dispersions of TiO_2 in 80/20 acetonitrile/H_2O at 20 percent by weight TiO_2

Dispersant	Dispersion concentration (percent wt./wt.)	State of dispersion
Tamol 731	1.0	Stable.
Do	2.0	Do.
Do	3.0	Do.
Tamol 850	1.0, 2.0, 3.0	Flocculated.
Tergitol 4	1, 3	Do.
Tergitol 7	1, 3	Do.
Hydroxyethyl cellulose	.50, .75, 1.0	Do.
Ethoquad	1.0, 2.0, 3.0	Do.
Ethomeen	1.0, 2.0, 3.0	Do.
Ethoduomeen	1.0, 2.0, 3.0	Do.
Ethofat	1.0, 2.0, 3.0	Do.

From the foregoing examples it can readily be seen that the delustered shaped articles of this invention are produced by forming a solution of an acrylonitrile polymer of at least about 85 weight percent acrylonitrile and up to about 15 weight percent of an ethylenically unsaturated compound copolymerizable with acrylonitrile in acetonitrile as the solvent, by uniformly dispersing a particulate delustrant in a mixture consisting essentially of a lower alkyl nitrile having from 2 to 4 carbon atoms and a dispersant which is a metal salt of a copolymer of a 1-olefin and a compound having the formula:



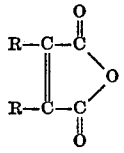
where R is individually selected from the group consisting of hydrogen, methyl and ethyl, forming a spinning solution by heating said acrylonitrile polymer and solvent under superatmospheric pressure to a temperature of from about 100 to 150 degrees centigrade, incorporating

the delustrant dispersion into the polyacrylonitrile spinning solution, maintaining said solution under superatmospheric pressure and at a temperature of from about 80 to 130 degrees centigrade, passing said solution through a shaped orifice into an evaporation zone maintained at a temperature below the pressure applied to said solution and releasing said superatmospheric pressure on said solution thereby forming said solution into a delustered shaped article.

While there have been described various embodiments of the present invention, the methods and products described herein are not intended to be understood as limiting the scope of the invention, as it is realized that changes therein are possible. It is intended that each element recited in any of the following claims is to be understood as referring to all equivalent elements for accomplishing substantially the same results in substantially the same or equivalent manner. It is intended to cover the invention broadly in whatever form its principles may be utilized, being limited only by the appended claims.

What is claimed is:

1. A solution consisting essentially of a fiber forming acrylonitrile polymer of at least 85 percent by weight acrylonitrile and up to 15 percent by weight of another ethylenically unsaturated compound copolymerizable therewith consisting essenting of from about 10 to 45 percent, by weight, of a particulate delustrant; from about 0.05 to 10 percent, by weight, of a particulate metal salt dispersant of a copolymer of a 1-olefin with from 4 to 16 carbon atoms and a compound having the formula:



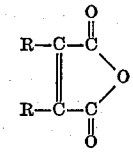
where R is individually selected from the group consisting of hydrogen, methyl and ethyl; and from about 46 to 89 percent, by weight of a lower alkyl nitrile having from 2 to 4 carbon atoms, containing up to about 50 weight percent water, wherein said particulate delustrant is substantially uniformly dispersed throughout the solution.

2. The solution of claim **1** wherein the particulate delustrant consists essentially of pigmentary TiO_2.

3. The solution of claim **1** consisting essentially of from about 15 to 30 percent by weight particulate delustrant, from about 1 to 5 percent by weight of the particulate metal salt dispersant of the copolymer and from about 60 to 80 percent by weight lower alkyl nitrile solvent.

4. The solution of claim **1** wherein the 1-olefin is diisobutylene and R is hydrogen.

5. A method for preparing a solution of fiber forming acrylonitrile polymer of at least 85 percent by weight acrylonitrile and up to 15 percent by weight of another ethylenically unsaturated compound copolymerizable therewith comprising substantially uniformly dispersing from about 10 to about 45 weight percent based on the weight of the dispersion of a particulate delustrant in a mixture consisting essentially of from about 46 to about 89 percent by weight based on the weight of the solvent of a lower alkyl nitrile having from 2 to 4 carbon atoms and containing up to about 50 weight percent water and from about 0.05 to about 10 percent by weight based on the weight of the solvent of a particulate metal salt dispersant of a copolymer of a 1-olefin with from 4 to 16 carbon atoms and a compound having the formula:



where R is individually selected from the group consisting of hydrogen, methyl and ethyl, and incorporating the delustrant dispersion into polyacrylonitrile spinning solution.

6. The method of claim **5** wherein the particulate delustrant consists essentially of pigmentary TiO_2.

7. The method of claim **5** wherein the particulate delustrant is incorporated into preformed polyacrylonitrile spinning solution.

8. The method of claim **5** wherein the particulate delustrant is incorporated into the spinning solution by first mixing the particulate delustrant with the particulate dispersant and the lower alkyl nitrile, then adding acrylonitrile polymer and forming the spinning solution.

9. The method of claim **1** wherein the solution consists essentially of from about 1 to 10 percent by weight particulate dispersant in the lower alkyl nitrile solvent.

10. The method of claim **5** wherein the 1-olefin is diisobutylene and R is hydrogen.

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