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SPINNING SOLUTIONS CONTAINING ACRYLONITRILE POLYMERS, DIMETHYLFORMAMIDE, AND AN ACETAL, AND PROCESS OF MAKING SAME

Ernst Pirot, Erlenbach (Main), Germany, assignor to Vereinigte Glanzstoff-Fabriken Aktiengesellschaft, Wuppertal-Elberfeld, Germany, a German joint-stock company

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This invention relates to spinning solutions containing acrylonitrile polymers and a method of preparing such solutions. More particularly, the invention is directed to spinning solutions of homopolymers, or copolymers of acrylonitrile which are dissolved in a mixture of dimethylformamide and an acetal.

Dimethylformamide is a well known and a suitable solvent for the production of fibers from acrylonitrile polymers. It has been observed, however that the structure of fibers obtained by spinning solutions of acrylonitrile polymers dissolved in dimethyl formamide was often detrimentally affected by that solvent. In the so-called wet spinning process wherein the solution of the acrylonitrile polymer in dimethyl formamide is coagulated by the action of a suitable coagulating agent the dimethylformamide which is still present in the freshly spun fibers possesses such a vigorous coagulation tendency that sometimes unsatisfactory formation of the fibers occurs. There are several fields wherein such fibers cannot be used.

It is therefore, an object of the instant invention to overcome these disadvantages and to provide the art with improved spinning solutions of acrylonitrile polymers.

A more particular object of the invention is to provide spinning solutions of acrylonitrile polymers comprising a mixture of dimethylformamide and an acetal as a solvent.

Among further objects of this invention are the provision of methods for the production of the spinning solutions for the acrylonitrile polymers.

A still further object of this invention is the production of synthetic fibers by spinning the solutions of acrylonitrile polymers dissolved in a mixture of dimethylformamide and an acetal.

These objects and further objects and attendant advantages which will appear in the more detailed description of the invention may be accomplished as follows:

According to this invention, it has been found that mixtures of dimethylformamide and at least one acetal are excellent solvents for acrylonitrile polymers; and that the solutions of such polymers in such mixtures of solvents are especially valuable for the production of synthetic fibers. Such spinning solutions may contain as acetals, for instance, an acetal obtained by the interaction of formaldehyde, acetaldehyde, their higher homologues as well as of benzaldehyde with monohydric or polyhydric alcohols such as methyl, ethyl, propyl, or n-butyl alcohol and their homologues or ethylene glycol or other polyhydric alcohols. Mixtures of different acetals with dimethylformamide may also be used. The solvent mixtures should contain dimethylformamide and a smaller amount of the acetal as for instance, from 5% to 15%; preferably from 8% to 12% acetal. When mixtures of different acetals are used in combination with dimethylformamide

their total amount should also lie between 5% and 15%, preferably between 8% and 12%. The spinning solution should usually contain for 100 parts by weight of the solvent mixture from 17.6 to 33.3 parts by weight of the acrylonitrile polymers.

The manufacture of the spinning solutions with the mixtures of dimethylformamide and at least one acetal may be carried out in the usual way. The acrylonitrile polymer which may be preferably in powdered form is mixed, for example, with the solvent mixture at low temperature to form a dispersion which is then heated to a higher temperature to form a homogeneous solution. The finely powdered acrylonitrile polymer may be introduced, for instance, at a temperature of 15° C. into a vacuum vessel which contains the solvent mixture through a bucket wheel while stirring. This mixture is then stirred at a temperature of about 15° C. or higher, but not exceeding 20° C. while deaerating until a finely distributed dispersion is obtained. The mixture is then gradually heated to 110° C. while stirring until a homogeneous ready-for-use spinning solution is obtained. The spinning solutions according to this invention are useful for the production of synthetic fibers by the known wet or the known dry spinning process. It is advantageous when the wet spinning process is carried out to coagulate the spinning solution of this invention more slowly than when coagulating a straight dimethylformamide solution so that markedly better formation of the fiber is achieved. At the same time the properties of the stretched fiber are improved so that they possess, after being stretched to from 4 to 10 times, markedly better textile characteristics. Similar improvements are obtained when the solutions are dry-spun by the process wherein the solvent mixture is evaporated during the spinning operation.

The terms "polymer of acrylonitrile" or "acrylonitrile polymer" used herein include both fiber or filament forming homopolymers and copolymers of acrylonitrile. Among the copolymers of acrylonitrile, those copolymers are preferred which contain at least 80% by weight of acrylonitrile and up to 20% by weight of another polymerizable compound such as acrylic acid amide, acrylic acid methyl ester, methacrylic acid methyl ester, fumaric acid dimethyl ester, vinylacetate, vinylimidazole, vinylcarbazole, vinylpyridine and methyl vinylketone.

The following examples illustrate this invention but the invention is not restricted to these examples. The parts are by weight.

Example 1

20 kg. of polyacrylonitrile having a K-value of 85 according to Fikentscher are dispersed at a temperature between 15° C. and 20° C. in a solvent mixture consisting of 72 kg. dimethylformamide and 8 kg. of dipropylformal while deaerating. The dispersion is gradually heated and forms at a temperature of between 110° C. and 120° C. a solution which may be spun according to the dry or the wet spinning process.

(*a*) *Dry spinning process.*—The dry spinning process is carried out in a dry spinning shaft having a length of 4 meters and an internal diameter of 300 mm. For the spinning, a counter current method is used wherein the direction of the stream of the drying gas is counter to the direction of the taken-off thread. The drying gas has a speed of 30 cm. per second and a temperature of 180° C. The thread is drawn with a velocity of 200 meters per minute.

(*b*) *Wet spinning process.*—The aforementioned spinning solution after being brought to a temperature of 120° C. is directly spun according to the wet spinning process using cold water (temperature of 18° C.) as the coagu-

lating agent. The formed thread may be drawn with a velocity of 150 to 400 meters per minute, and effectuating simultaneously a pre-stretching of the thread. The thus obtained filament has a high lustre as contrasted with that of filament spun from a solution containing dimethylformamide as sole solvent. This high lustre indicates good orientation of the filament. The threads are then stretched from 5 to 8 times their original length without any difficulty, the extent of this stretching being dependent upon the prior pre-stretching.

Example 2

In accordance with Example 1, 22 kg. of polyacrylonitrile with a K-value of 80 are dissolved in a solvent mixture consisting of 88% by weight of dimethylformamide and 12% by weight of dibutylformal. This solution may be processed to form synthetic fibers in accordwith Examples 1(*a*) and 1(*b*) either by the dry or by the wet spinning method.

Example 3

19 kg. of a copolymer of 90% acrylonitrile and 10% of acrylic acid amide with a K-value of about 90 are dissolved in 81 kg. of a solvent mixture consisting of 92% dimethylformamide and 8% of dibutyl acetal (obtained by interaction of acetaldehyde and n-butanol). Threads are spun from the solution as in Example 1(*b*). After the usual stretching the threads have a tensile strength of 30 "Reisskilometer" at an elongation of 30% to 35%.

Example 4

19.5 kg. of polyacrylonitrile with a K-value of 88 are dissolved as in Example 1 in 80.5 kg. of a mixture of 93% by weight of dimethylformamide, 4% by weight of dipropylformal and 3% by weight of dibutyl acetal so that a ready-for-use spinning solution is obtained. Threads are produced from the solution in accordance with the method of Example 1(*a*). The filaments, after being stretched to 9 times their original length, have a tensile strength of 38 "Reisskilometer" at an elongation of 21%.

Example 5

20 kg. of a copolymer (K-value of 88) formed from 88% of acrylonitrile, 8% of methacrylic acid methyl ester and 4% of vinyl acetate, are dispersed at a temperature between 15° C. and 20° C. in 80 kg. of a mixture of 90% dimethylformamide and 10% of dibutyl acetal while deaerating. From this mixture a spinning solution is prepared as in Example 1 which is spun into threads by the wet spinning process in accordance with Example 1(*b*). The threads are stretched to 8 times their original length, and have a tensile strength of 40 "Reisskilometer" at an elongation of 21% (1 Reisskilometer=⅛ g./den.).

It will be understood that the foregoing description of the invention and the examples set forth are merely illustrative thereof. Accordingly, the appended claims are to be construed as defining the invention within the full spirit and scope thereof.

I claim:

1. A spinning solution of a polymer selected from the class consisting of homopolymers of acrylonitrile and copolymers of a monomeric mixture of which at least 80 percent is acrylonitrile and the balance is an ethylenically unsaturated compound comprising as the solvent a mixture of 85–95 parts dimethylformamide and 15–5 parts of at least one acetal of an aldehyde which is a member of the group consisting of formaldehyde and acetaldehyde and a lower monohydric alkanol having from 1 to 4 carbon atoms.

2. A spinning solution in accordance with claim 1 wherein the solvent is a mixture of at least 88 percent to 92 percent by weight of dimethylformamide and of from 12 percent to 8 percent by weight of the acetal.

3. A spinning solution in accordance with claim 1 wherein the polymer is polyacrylonitrile.

4. A spinning solution in accordance with claim 1 wherein the polymer is polyacrylonitrile and the solvent is a mixture of dimethylformamide and dibutylformal.

5. A spinning solution in accordance with claim 1 wherein the solvent is a mixture of dimethylformamide, dipropylformal and dibutyl acetal.

6. A spinning solution in accordance with claim 1 wherein the polymer is polyacrylonitrile and the solvent is a mixture of dimethylformamide, dipropylformal and dibutyl acetal.

7. A spinning solution in accordance with claim 1 wherein the polymer is a copolymer of 90 percent acrylonitrile and 10 percent of acrylic acid amide.

8. A spinning solution in accordance with claim 7 wherein the solvent is a mixture of 92 percent dimethylformamide and 8 percent of dibutyl acetal.

9. A process for the manufacture of a spinning solution of a polymer selected from the class consisting of homopolymers of acrylonitrile and copolymers of a monomeric mixture of which at least 80 percent is acrylonitrile and the balance is an ethylenically unsaturated compound which comprises dissolving the said polymer in a mixture of from 85 percent to 95 percent by weight of dimethylformamide and from 15 percent to 5 percent by weight of an acetal of an aldehyde which is a member of the class consisting of formaldehyde and acetaldehyde and a lower monohydric alkanol.

10. A process in accordance with claim 9 wherein the polymer is polyacrylonitrile.

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