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STABILIZED SOLUTIONS OF ACRYLONITRILE POLYMERS AND STABILIZED SOLVENT

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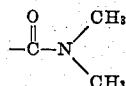
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This invention relates to stabilized solutions of acrylonitrile polymers, and to a stabilized solvent for these polymers.

This application is a continuation-in-part of our copending applications Serial No. 49,651, Serial No. 49,652, and Serial No. 49,653, all filed September 16, 1948. Serial No. 49,651 issued as U. S. Patent 2,629,711 on February 24, 1953, and Serial No. 49,652 issued as U. S. Patent 2,629,712 on the same date.

It is known that solutions of polymers of acrylonitrile can be prepared by dissolving such polymers in various organic solvents or in aqueous solutions of certain inorganic metal salts. These solutions have been found to be readily adaptable for spinning into fibers or in the manufacture of film. Since the metal salts have a tendency to deposit on the filaments during the spinning operation, and removal thereof during the passage of the filaments through the spinning bath leaves numerous voids or weak spots in the fibers, metal salts have not proved to be entirely satisfactory in the preparation of synthetic fibers. Difficulties are also encountered when organic solvents are used in the spinning of fibers from solutions of polymers of acrylonitrile. Yet particles frequently form, thus either clogging the spinnerets or giving a fiber of low tensile strength. Also the color of the fibers spun from many of the solvents heretofore used does not meet the standards demanded of a product in a competitive market.

Houtz U. S. Patent 2,404,713, dated July 23, 1946 and Latham U. S. Patent 2,404,714 dated July 23, 1946, describe processes for preparing solutions of polymers of acrylonitrile suitable for spinning into fibers which comprises dissolving the polymer in an organic compound contain-



group e. g., N,N-dimethylformamide. These solvents provide a convenient medium from which fibers can be spun, however there is some tendency for the polymers containing acrylonitrile to "ball" or form large gel particles therein. To overcome this difficulty, it has been proposed to add gaseous anhydrides to the cooled solvent containing the polymer to obtain a uniform dispersion of the polymer in the vehicle, and then gradually warm the dispersion to a temperature of 100°-130° C., while solution is effected and the gaseous anhydride is expelled from the solu-

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tion (Finzel U. S. Patent 2,404,728, dated July 23, 1946).

It is an object of this invention to provide stabilized solutions of polymers of acrylonitrile which are substantially clear, colorless, and gel-free.

Another object is to provide a method for obtaining these solutions.

Still another object is to provide a stabilized solvent for polymers of acrylonitrile.

A further object is to provide white, lustrous fibers from such solutions and a process for preparing such fibers. Other objects will become apparent from a consideration of the following description and examples.

The above objects are directed to the stabilization of solutions of polymers of acrylonitrile in N,N-dimethylacetamide, and to the stabilization of the N,N-dimethylacetamide.

According to our invention we accomplish the above objects by intermixing or commingling a polymer of acrylonitrile containing in the polymer molecule at least 80 per cent by weight of acrylonitrile with N,N-dimethylacetamide containing certain inorganic or organic acids, or anhydrides. These inorganic or organic acids, or anhydrides, stabilize the N,N-dimethylacetamide, a substance which undergoes spontaneous decomposition as evidenced by its increasing alkalinity on standing. The presence of the polymers of acrylonitrile seems to have a catalytic effect on the decomposition of the N,N-dimethylacetamide, which effect is arrested by the inorganic or organic acids, or anhydrides, of our invention.

As organic acids we can use oxalic acid, acetic acid, trifluoroacetic acid, alkane sulfonic acids, aromatic sulfonic acids, alkyl phosphoric and phosphorous acids, alkane phosphonic acids and alkene sulfonic acids. Typical alkane sulfonic acids include methanesulfonic, ethanesulfonic, propane-1-sulfonic, propane-2-sulfonic, n-butane-1-sulfonic, isobutane-1-sulfonic, sulfoacetic, β -hydroxy-ethylsulfonic, etc. acids (e. g. alkane sulfonic acids containing from 1 to 4 carbon atoms). Typical aromatic sulfonic acids include benzenesulfonic, p-toluenesulfonic, o-toluenesulfonic, m-benzenedisulfonic, 1,3,5-benzenetrisulfonic, etc. acids (e. g. a sulfonic acid of the benzene series). Other useful aromatic sulfonic acids include naphthalene- α -sulfonic, naphthalene- β -sulfonic, 1,5-naphthalenedisulfonic, 2,6-naphthalenedisulfonic, etc., acids (e. g. a sulfonic acid of the naphthalene series). Typical alkyl phosphoric acids include mono-

methyl acid orthophosphate, monoethyl acid orthophosphate, mono-n-propyl acid orthophosphate, monoisopropyl acid orthophosphate, mono-n-butyl acid orthophosphate, monoisoamyl acid orthophosphate, mono-n-octyl acid orthophosphate, mono-n-capryl acid orthophosphate, dimethyl acid orthophosphate, diethyl acid orthophosphate, ethyl isoamyl acid orthophosphate, ethyl n-octyl acid orthophosphate, ethyl n-capryl acid orthophosphate, di-n-butyl acid orthophosphate, n-butyl n-amyl acid orthophosphate, dimethyl acid pyrophosphate, diethyl acid pyrophosphate, di-n-propyl acid pyrophosphate, diisopropyl acid pyrophosphate, di-n-butyl acid pyrophosphate, diisoamyl acid pyrophosphate, di-n-octyl acid pyrophosphate, di-n-capryl acid pyrophosphate, etc. (See Alder & Woodstock "Chem. Ind.," vol II (1942), pg. 516.) Typical alkyl phosphorous acids include: monomethyl acid phosphite, monoethyl acid phosphite, mono-n-propyl acid phosphite, monoisopropyl acid phosphite, monoisobutyl acid phosphite, monoisoamyl acid phosphite, dimethyl acid phosphite, diethyl acid phosphite, di-n-propyl acid phosphite, diisopropyl acid phosphite, di-n-butyl acid phosphite, diisobutyl acid phosphite, monoethyl acid hypophosphite, monoisobutyl acid hypophosphite, etc. Alkyl phosphoric and phosphorous acid (i. e. alkyl acid esters of acids of phosphorus) containing from 1 to 10 carbon atoms in the alkyl group have been found to be especially useful. Alkyl acid esters of acids of phosphorus containing from 1 to 5 atoms in the alkyl group constitute a preferred class. Typical alkane phosphonic acids include methane phosphonic, ethane phosphonic, n-propane phosphonic, isobutane phosphonic (isobutyl phosphonic), isopentane phosphonic (isoamyl phosphonic), etc. acids (e. g. alkane phosphonic acids containing from 1 to 5 carbon atoms). Typical alkene phosphonic acids include: vinyl phosphonic, propene-2-phosphonic, α -phenylvinyl phosphonic, etc. acids (e. g. α,β -unsaturated, alkene phosphonic acid containing from 2 to 8 carbon atoms in the alkene group). Alkene phosphonic acids useful in practicing our invention are described in U. S. Patent 2,365,466, dated December 19, 1944. The advantages obtained with one or more of the above acids do not extend to organic acid generally we have found. For example, succinic, adipic, trichloroacetic, propionic, etc. acids do not provide the improvements which have been observed when the acids enumerated above are used.

As inorganic acids we can use the oxygen acids of phosphorus (i. e. metaphosphoric, orthophosphoric, hypophosphoric, pyrophosphoric, metaphosphorous, orthophosphorous, hypophosphorous or pyrophosphorous acid). As anhydrides we can advantageously use those of the oxygen acids of phosphorus, i. e. oxides of phosphorus, such as phosphorus trioxide (P_2O_3), phosphorus tetraoxide (P_2O_4) and phosphorus pentoxide (P_2O_5). The advantages obtained with one or more of the above acids or oxides of phosphorus do not extend to inorganic acids or anhydrides generally, we have found. For example, the hydrohalogen acids (e. g. hydrochloric, hydrobromic, etc. acids), nitric acid, persulfuric acid, etc., do not provide the improvements which we have obtained with our new solutions of polymers of acrylonitrile.

The quantity of acid or anhydride used varies and is generally a function of the particular acid

or anhydride employed. For the purposes of our invention we have found that from 0.1 to 5.0 per cent by weight, based on the weight of solvent, of acid (or anhydride) is adequate. Larger or smaller quantities of acid (or anhydride) can be used, although there is ordinarily no advantage in using amounts other than those indicated above.

Instead of employing the acids themselves in our process, we can form the acid in situ, as for example, by adding an anhydride of the acid to the solvent. Since the solvent generally contains a small amount of water, the water reacts with the anhydride to form the free acid. This method of procedure also serves as a convenient means for dehydrating the solvent and increasing the dissolving power of the solvent for the polymer. The term "acid" as used in the following description is intended to define both the free acid and its anhydride.

Advantageously we can effect solution of the polymers of acrylonitrile by applying a small amount of heat to the mixture of the acid, polymers and solvent. Since the acids used in our invention increase the dissolving power of the solvents to such a marked degree, it is not essential that the mixture be heated. Heat does serve to shorten the time required to effect solution. Care should be taken not to heat the mixture for prolonged periods of time, since heating lowers the color characteristics of fibers spun from heated solutions. The effect of prolonged heating on the solutions obtained according to the process of our invention is not as deleterious as that which results when solutions containing no acid are so heated. In order to obtain uniform solutions according to methods heretofore employed, the dispersion of polymer has to be subjected to high temperatures for a time. This heating caused a diminution in desirable color properties in the solution, which are passed along during the spinning to the fibers formed. This heating can be largely or entirely avoided in our invention, however, thus providing fibers which are white and lustrous.

The inorganic gaseous anhydrides previously added to N,N-dimethylformamide were for the purpose of reducing the dissolving power of this solvent for the polymers of acrylonitrile, so that a dispersion could be obtained. The acids (or anhydrides) used in this invention are in contradistinction thereto for the purpose of increasing this dissolving power of the solvent for the polymer. Whereas the polymers used according to the older, less efficacious methods had to be ground to minute particle size, the polymer used in this invention can be 20-mesh size or larger, with little or no apparent tendency to "balling" or the formation of gel particles. The solutions obtained in our invention are more stable than those obtained heretofore and show less tendency to gel, or develop color on standing.

The amount of polymer dispersed in the solvent can be varied depending on the intended use of the polymer solution and the molecular weight of the polymer; i. e. larger quantities of lower molecular weight polymers must be added to give a viscosity comparable to that obtained with a given amount of a higher molecular weight polymer. Although our invention is not to be limited thereby, generally our solutions can contain from about 2 to 25 per cent by weight of the polymer, based on the weight of the solvent. The molecular weight of the polymers used herein vary from about 50,000 to 500,000.

although polymers having a molecular weight as low as 25,000 or as high as 750,000 can be used to advantage.

In our applications Ser. No. 49,651, Ser. No. 49,652, Ser. No. 49,653, all filed on September 16, 1948, we have described methods for preparing polymers of acrylonitrile having improved solubility characteristics, and whose solutions can be spun into white, lustrous fibers, comprising polymerizing acrylonitrile in the presence of a persulfate polymerization catalyst e. g. ammonium persulfate, etc.), a water-soluble, sulfur-containing catalyst activator (e. g. sodium bisulfite, etc.) and certain types of acids, both inorganic and organic. Whereas the methods described in our copending applications provide improvements in the properties of acrylonitrile polymers, solutions of such polymers, and fibers prepared therefrom, and the present invention provides a convenient and efficacious method for preparing water-clear, gel-free solutions and white, lustrous fibers from polymers prepared according to prior art methods, we have found that the present invention provides solutions of polymers of acrylonitrile, and fibers prepared therefrom, having even more markedly improved properties when the solutions and fibers prepared according to the process described herein are obtained from polymers of acrylonitrile prepared according to the processes described in our applications Ser. No. 49,651, Ser. No. 49,652 and Ser. No. 49,653. That is to say, by applying the improved process of this invention to the improved methods for preparing polymers of acrylonitrile, described in our copending applications, solutions and fibers of polymers of acrylonitrile of particularly outstanding properties can be obtained.

The following examples will illustrate more fully the manner whereby we practice our invention.

EXAMPLE 1

20 g. of freshly distilled acrylonitrile were added to 200 cc. of distilled water containing 1.1 cc. of sulfuric acid (s. g. 1.84) in a 240 cc. screw-cap bottle. The mixture was thoroughly shaken until the water was saturated with monomer. To this solution were added 0.8 g. of sodium bisulfite and 0.4 g. of ammonium persulfate, the cap screwed on tightly and the mixture shaken again. The bottle was placed on a tumbling wheel which revolved at five revolutions per minute and tumbled at room temperature for 18 hours. The polymer was then filtered off, washed thoroughly with distilled water and dried. The yield was 18.8 g. of pure white powder.

EXAMPLE 2

20 g. of acrylonitrile were polymerized according to the method set forth in Example 1 above, except that 1.4 cc. of concentrated nitric acid were employed in place of the sulfuric acid. After drying, the yield of polymer 18.9 g.

EXAMPLE 3

20 g. of acrylonitrile were polymerized according to the method set forth in Example 1 above, except that 1.8 cc. of concentrated hydrochloric acid were employed in place of the sulfuric acid. After drying, the yield of polymer was 19.6 g.

EXAMPLE 4

20 g. of acrylonitrile were polymerized according to the method set forth in Example 1 above, except that 1.2 cc. of formic acid were employed

in place of the sulfuric acid. After drying, the yield of polymer was 18.8 g.

EXAMPLE 5

20 g. of acrylonitrile were polymerized according to the method set forth in Example 1 above, except that 1.38 cc. of glacial acetic acid were used in place of the sulfuric acid. After drying, the yield of polymer was 18.6 g.

Solutions of the acrylonitrile polymers obtained in the above examples were prepared by dispersing 1.0 g. of the polymer in 20 cc. of N,N-dimethylacetamide, adding 0.5 per cent of phosphorus pentoxide, and stirring until solution was effected. To detect the stabilizing effect of the phosphorus pentoxide the solutions were heated at 100° C. for the periods of time indicated in the table below, and the blue light transmission of the solutions measured as a means of determining the extent of solution and detection of any discoloration present, since blue light was more highly absorbed in a discolored solution than the other colors of the spectrum. The results are given in the following table:

Table I

Solution from Polymer of—	Stabilizing Agent	Blue Light Transmission—Percent			
		5 min.	10 min.	3.0 min.	60 min.
Example 1.....	none	93	89	80	68
Do.....	P ₂ O ₅	98	97	95	92
Example 2.....	none	87	81	75	64
Do.....	P ₂ O ₅	96	95	93	91
Example 3.....	none	93	87	79	66
Do.....	P ₂ O ₅	96	95	93	90
Example 4.....	none	93	88	79	65
Do.....	P ₂ O ₅	96	95	94	91
Example 5.....	none	92	86	76	64
Do.....	P ₂ O ₅	95	94	92	90

The above measurements were all based on the transmission of pure N,N-dimethylacetamide which was set at 100 per cent. It can thus be seen that the addition of a small amount of phosphorus pentoxide produces a beneficial effect upon the polymer solutions. While the blue light transmission of the solutions containing no phosphorus pentoxide was high after only five minutes heating, at the end of one hour's heating at 100° C. not one of the unstabilized solutions had a blue light transmission as high as 70 per cent while the lowest blue light transmission for the stabilized solutions was 90 per cent. The heating accelerates the discoloration of the unstabilized solutions to a marked degree, while having little effect on the stabilized solutions. The effect of heating illustrates what can be expected in the spinning of fibers from the solutions, or upon prolonged storage thereof. A limited amount of heating has a beneficial effect, while prolonged heating has the discoloration effect shown above.

Heating also causes the solutions containing no added acid or anhydride to gel in a relatively short period of time as shown in the following table. Since heat is generally used to shorten the time required to effect solution of the polymers, it can be seen that the disadvantages caused through the use of heat present a formidable problem in the spinning operation of solutions of polymers into fibers, because of the accelerated formation of gel particles, and the obtention of white, lustrous fibers from solutions subjected to the influences of heat. Solutions of the polymers obtained in the above examples were prepared by dispersing 1.0 g. of the polymer in

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20 cc. of N,N-dimethylacetamide, adding 0.5 per cent of phosphorus pentoxide and stirring at room temperature until solution was effected. The solutions were then heated at 120° C. and the time required for the solution to gel was observed. The observed time is given in the following table as gel-time.

Table II

Solution of Polymer of—	Stabilizing Agent	Gel-time in hours ¹
Example 1.....	none	40
Do.....	P ₂ O ₅	148
Example 2.....	none	42
Do.....	P ₂ O ₅	140
Example 3.....	none	38
Do.....	P ₂ O ₅	144
Example 4.....	none	46
Do.....	P ₂ O ₅	148
Example 5.....	none	44
Do.....	P ₂ O ₅	150

¹ The values given are not absolute, due to the eccentricity of the polymer solutions, the gelling times varying slightly from one batch of polymer to another.

From the data given it can be seen that the presence of phosphorus pentoxide in the solution serves to stabilize the solution against gelling to an extent not heretofore obtainable.

In a manner similar to that illustrated above, solutions of the acrylonitrile polymers obtained in Examples 1 to 5 were prepared by dispersing 1.0 g. of the polymer in 20 cc. of N,N-dimethylacetamide, adding 1.0 per cent of the acids listed below (based on the weight of the N,N-dimethylacetamide), and stirring until solution was effected. The blue light transmission of the solutions was then measured as a means of determining the extent of solution and detection of any irregularities present. The measurements were based on the blue light transmission of pure N,N-dimethylacetamide which was set at 100 per cent. The results are given in the following table.

Table III

Solution of Polymer of—	Blue Light Transmission—Percent					
	Control	Acid A	Acid B	Acid C	Acid D	Acid E
Example 1.....	89	97	95	97	99	95
Example 2.....	81	96	94	96	97	93
Example 3.....	87	95	94	96	95	94
Example 4.....	88	95	93	95	96	93
Example 5.....	86	94	92	94	95	92

Acid A=orthophosphoric acid.
Acid B=ethanesulfonic acid.
Acid C=oxalic acid.
Acid D=trifluoroacetic acid.
Acid E=ethanephosphonic acid.

While immediate improvement can be observed due to the addition of the above acids (or anhydrides), as shown by the data in Table I, the improvement becomes more marked as the solutions are aged. As shown by Table II, the acids or anhydrides stabilize the polymer solutions against undesirable gelling, which would prevent utilization of the solutions in the spinning of fibers.

By replacing the oxalic acid used in Table III with a molecularly equivalent amount of acetic anhydride, a solution which is stable to long periods of heating can be obtained.

In a manner similar to that illustrated other acids or anhydrides selected from those set forth above can be employed to advantage. For example, the ethanesulfonic acid in Table III can be replaced by molecularly equivalent amounts

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of aromatic sulfonic acids (e. g. benzenesulfonic acid, p-toluenesulfonic acid, etc.) to give useful solutions of polymers of acrylonitrile. In like manner the ethanephosphonic acid can be replaced by molecularly equivalent amounts of alkyl acid esters of acids of phosphorus (e. g. monomethyl acid phosphite, diethyl acid phosphite, diisobutyl acid phosphite, etc.).

Although our invention has been found to be especially useful in the preparation of solutions of the homopolymer of acrylonitrile, solutions of interpolymers of acrylonitrile with other interpolymerizable compounds, e. g. acrylic acid, acrylamide, ethyl acrylate, vinyl acetate, vinyl chloride, styrene, etc. can also be prepared. The interpolymers used should generally contain at least 80 per cent by weight of acrylonitrile in the polymer molecule, since polymers containing less than this amount melt at too low temperatures to warrant their use in the preparation of commercial products, such as fibers or yarns. Generally from 6 to 9 per cent by weight of the other polymerizable material in the interpolymer is adequate for the purposes of our invention. Interpolymers containing less than 80 per cent by weight of acrylonitrile in the polymer molecule (e. g. from 70 to 75 per cent) also can be advantageously utilized in the preparation of our polymer solution. These interpolymers are useful where an unusually high melting polymer is not required, as for example, in the preparation of films or sheets.

Although the reasons for the unexpected behavior and properties of the solutions of our invention are not fully understood, it appears that, at least in part, these phenomena are associated with a reduction in alkalinity of the solvent. Hydrocyanic acid is apparently released from the polymer under strongly alkaline conditions thus causing discoloration of the solutions. The stabilizing effect of the above acids or anhydrides on N,N-dimethylacetamide, and solutions of polymers therein, also appears in part to be due to a reduction of free amine in the N,N-dimethylacetamide. Salt formation appears to play only a small part, however, since such small amounts of acids or anhydrides stabilize effectively. The amount of acids, or anhydrides, added are not generally sufficient to neutralize all free amine and also form acid-addition salts with the large amount of amide present. Small amounts of acid, or anhydride, cause a marked lowering in the pH of the amide, and this lowering is in some manner associated with the stabilization effect observed. The acid, or anhydride, arrests the alkalinity of the N,N-dimethylacetamide, which would progressively increase in the absence of the stabilizing agent.

This increase in alkalinity on standing renders the N,N-dimethylacetamide a poor solvent for polymers which are readily hydrolyzed, such as polyvinyl formate, polyvinyl acetate, polyvinyl trifluoroacetate, etc. Solutions of these polymers in the amide undergo hydrolysis with the formation of insoluble polyvinyl alcohol, which precipitates out. The unstabilized solvent is thus of little value from a practical standpoint in the preparation of spinning or coating solutions from these polymers.

N,N-dimethylacetamide which has been stabilized with a small amount of the above acids or anhydrides is entirely satisfactory as a solvent for these easily hydrolyzed polyvinyl esters, since no separation of insoluble polyvinyl alcohol is apparent after prolonged storage.

While the pH of N,N-dimethylacetamide varies from 8.6 to 9.2, or even higher as aging progresses, we have noted that as small an amount as 0.5 per cent of phosphorus pentoxide reduces the pH to about 3.0 and prevents the pH from rising substantially higher than this figure. As noted above, the advantages of our invention have not been found to extend to all acids; or anhydrides. Because of this fact, the simple reduction in pH of the N,N-dimethylacetamide does not explain all of the phenomena of our invention.

What we claim as our invention and desire secured by Letters Patent of the United States is:

1. As a new composition of matter, a stabilized solution of a polymer of acrylonitrile, containing in the polymer molecule at least 80 per cent by weight of acrylonitrile, in N,N-dimethylacetamide, said solution containing from 0.1 to 5.0 per cent by weight, based on the weight of the N,N-dimethylacetamide, of an inorganic oxygen acid of phosphorus.

2. As a new composition of matter, a stabilized solution of a polymer of acrylonitrile, containing in the polymer molecule at least 80 per cent by weight of acrylonitrile, in N,N-dimethylacetamide, said solution containing from 0.1 to 5.0 per cent by weight, based on the weight of the N,N-dimethylacetamide, of orthophosphoric acid.

3. As a new composition of matter, a stabilized solution of a homopolymer of acrylonitrile in N,N-dimethylacetamide, said solution containing from 0.1 to 5.0 per cent by weight, based on the weight of the N,N-dimethylacetamide, of an inorganic oxygen acid of phosphorus.

4. As a new composition of matter, a stabilized solution of a homopolymer of acrylonitrile in N,N-dimethylacetamide, said solution containing from 0.1 to 5.0 per cent by weight, based on the weight of the N,N-dimethylacetamide, of orthophosphoric acid.

5. As a new composition of matter, a stabilized solution of a polymer of acrylonitrile, containing in the polymer molecule at least 80 per cent by weight of acrylonitrile, in N,N-dimethylacetamide, said solution containing from 0.1 to 5.0 per cent by weight, based on the weight of the N,N-dimethylacetamide, of hypophosphorous acid.

6. As a new composition of matter, a stabilized solution of a homopolymer of acrylonitrile in N,N-dimethylacetamide, said solution containing from 0.1 to 5.0 per cent by weight, based on the weight of the N,N-dimethylacetamide, of hypophosphorous acid.

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