Patented Apr. 11, 1950

2,503,244

UNITED STATES PATENT OFFICE

2,503,244

SOLUTIONS OF ACRYLONITRILE POLYMERS

Harry W. Coover, Theodore E. Stanin, and Joseph B. Dickey, Rochester, N. Y., assignors to Eastman Kodak Company, Rochester, N. Y., a corporation of New Jersey

No Drawing. Application September 16, 1948, Serial No. 49,654

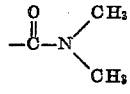
10 Claims. (Cl. 260—32.6)

1

This invention relates to solutions of acrylonitrile polymers and to a process for preparing such solutions.

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 a process for preparing solutions of polymers of acrylonitrile suitable for spinning into fibers which comprises dissolving the polymer in an organic compound containing a



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

Despite the improvements which have been

2

realized in the art, white, lustrous fibers have not heretofore been obtainable from solutions of polymers of acrylonitrile, nor have the solutions of the polymers been colorless, clear and gel-free to the degree necessary for a commercial product.

It is an object of this invention to provide substantially clear, colorless and gel-free solutions of polymers of acrylonitrile. Another object is to provide a process for obtaining such solutions. Still another 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.

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-dimethylformamide or N,N-dimethylacetamide, in the presence of certain inorganic acids or anhydrides. The solutions so obtained are substantially water-clear and colorless, and are in addition substantially free of gel particles. Fibers spun from solutions prepared according to our invention are lustrous and white, and of uniform strength or tenacity.

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 characteristic 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 the 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, and Ser. No. 49,653, all filed on even date herewith, 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

10.0 g. of freshly distilled acrylonitrile, 1 cc. of 10 per cent hydrogen peroxide and 1 cc. of 6N sulfuric acid were added to 90 cc. of distilled water in which 0.2 g. of $FeSO_4.7H_2O$ had been dissolved. Polymerization began almost immediately as evidenced by the formation of a fine, powdery precipitate. The polymerization was complete in 3 to 4 hours at room temperature. The polymer was filtered off, washed free of acid and iron with distilled water and dried.

EXAMPLE 2

8.0 g. of freshly distilled acrylonitrile, 2.0 g. of acrylamide and 1 cc. of 10 per cent hydrogen peroxide were added to 90 cc. of distilled water. The mixture was heated at 60° C. for 24 hours, and the polymer which had precipitated was filtered off, washed with distilled water and dried.

EXAMPLE 3

10.0 g. of freshly distilled acrylonitrile, 0.4 g. of sodium bisulfite and 0.2 g. of ammonium persulfate were added to 90 cc. of distilled water. The polymerization started immediately at room temperature and was complete within 3 to 4 hours. The polymer which had precipitated was filtered off, washed with distilled water and dried.

Solutions of the polymers obtained in the above examples were prepared by dispersing 1.0 g. of the polymer in 20 g. of N,N-dimethylformamide, adding a quantity of acid in the amount given in the table below, and stirring until solution was effected. The transmission of light by the solutions of polymers was then measured. The amount of transmission proved to be a reliable means for measuring the extent of solution

and the detection of any irregularities present. The blue light transmission was particularly a useful method for illustrating solution properties, 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

Polymer of Example	Acid or Andydride	Quantity of Acid or Anhydride [b]	Transmission, per cent					
			Blue	Green	Orange	Red	Blue-green	Violet
		Per cent						
1	none	none	20	52	71	69	45	44
1[a]	do	do	2	4	5	4	3	3
1	H_3PO_4	2	90	92	91	92	91	90
1[a]	do	2	74	83	90	90	83	79
2	none	none	26	57	76	75	51	60
2	H_3PO_4	1	56	86	90	92	83	89
3	none	none	50	62	81	82	55	54
3	P_2O_5	0.2	98	100	100	100	99	98
3	H_3PO_4	0.2	94	96	95	96	95	94

[a] The solution was heated for 3 hours at 110° C. before the transmission was measured.
[b] Based on the weight of solvent used.

The above measurements were all based on the transmission of pure N,N-dimethylformamide which was set at 100 per cent It can thus be seen that the addition of a small quantity of one of the acids (or anhydrides) set forth above produces a beneficial effect upon the polymer solutions. While heating the solution causes a reduction in the transmission of light, both in the case of the solution containing no acid and in the case of solutions containing an acid, the effect is much greater in the case of the solutions which contain no added acid, further lowering the light transmission of the solutions whose transmission prior to heating leaves much to be desired.

Heating also causes the solutions containing no added acid to gel in a relatively short period of time as shown in the table below 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 presents a formidable problem both 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 2.0 g. of the polymer in 20 g. of N,N-dimethylformamide, adding an acid (or anhydride) in the amount given in the table below, and stirring at room temperature until solution was effected. The solutions were then heated at 110° C., and the time required for the solution to gel was observed. The observed time is given as the gel-time.

Table II

Polymer of Example	Acid or Anhydride	Quantity of Acid or Anhydride [a]	Gel-Time [b]
		Percent	*Hours*
1	none	none	<10
1	H_3PO_4	1	>60
2	none	none	<10
2	P_2O_5	0.1	>60
3	none	none	<10
3	H_2PO_4	2	>60

[a] Based on the weight of solvent.
[b] 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 above it can be seen that the presence of an acid in the solution serves to stabilize the solution against gelling to an extent not heretofore obtainable.

EXAMPLE 4

32 g. of sulfuric acid (sp. grav. 1.84) and 66.7 g. of a 30 per cent aqueous solution of hydrogen peroxide were dissolved in 10 liters of distilled water, and the mixture was degassed by refluxing at reduced pressure (20 mm.). While stirring the solution 1000 cc. of freshly distilled acrylonitrile were added. About 300 cc. of the acrylonitrile remained undissolved. The air in the reaction vessel was displaced by passing in gaseous nitrogen, and 34 g. of crystalline green ferrous sulfate ($FeSO_4.7H_2O$) were added. The reaction mixture was stirred intermittently as the polymer formed to dissolve the acrylonitrile monomer which remained undissolved. After 16 hours, the reaction mixture was filtered, and the filter cake was washed free of acid and iron. After drying, there were obtained 790 g. of polymer.

Several 0.1 g. portions of the polymer obtained in Example 4 were suspended in 10 cc. portions of N,N-dimethylformamide to give a 1 per cent solution of the polymer. 0.1 g. of the acids given in the table was added to the suspensions which were stirred at room temperature. The transmission of blue light of the various solutions was then measured, the results of which are given in the following table:

Table III

Acid Used	Transmission of Blue Light, Per cent
None	45
Hypophosphorous	64
Orthophosphorous	63

It can be seen from the above table that the acids employed improve the color characteristics of the polymer solutions and consequently films or fibers prepared therefrom.

EXAMPLE 5

90 gms. (1 mole) of oxalic acid were dissolved in 9 liters of distilled water, and the solution was added to a 3-necked, 12-liter flask which was equipped with a gate type, stainless steel stirrer. The air in the flask was replaced with nitrogen gas and 900 gms. (17 moles) of freshly distilled acrylonitrile were then added. The mixture was stirred and about 75 per cent of acrylonitrile

went into solution. While the solution was slowly stirred, 18 gms. (0.079 mole) of ammonium persulfate and 36 gms. (0.35 mole) of sodium bisulfite were added and dissolved. The polymerization began almost immediately as evidenced by the formation of a fine, white precipitate. The solution was stirred from time to time to aid in dissolving the unsolubilized portion of the acrylonitrile and the dissipation of the small amount of heat released during the polymerization. After all of the monomeric material had been dissolved the stirring was discontinued. At the end of 18 hours the reaction mixture was filtered with the aid of suction, and the filter cake was washed free of acid with distilled water and then dried. There were thus obtained 820 gms. of pure polyacrylonitrile, having an intrinsic viscosity of 1.96, as measured in a 0.25 per cent by weight solution of the polymer in dimethylformamide.

EXAMPLE 5A

60 g. of the polymer obtained in Example 5 above were added to a suspension of 2.5 g. of phosphorus pentoxide in 500 cc. of N,N-dimethylformamide while stirring at room temperature. The air above the suspension was displaced by passing in nitrogen gas. After stirring the mixture for 1 hour only a few of the larger polymer particles remained undissolved. These particles were dissolved by heating the solution in an oil bath at 75° C. for 15 minutes. There was thus obtained a substantially water-clear, viscous solution (dope) of the polymer.

EXAMPLE 5B

200 g. of powdered "dry ice" (carbon dioxide) were mixed intimately with 60 g. of the polymer obtained in Example 5 above, and 500 cc. of N,N-dimethylformamide were added slowly to the mixture with stirring. A slurry of the polymer formed, and the polymer slowly dissolved as the temperature of the N,N-dimethylformamide approached room temperature. Complete solution of the polymer was effected by heating the solution containing undissolved particles on an oil bath at 130°. The viscous solution of polymer so obtained was light amber in color and was substantially free from swollen particles.

The light transmission of the solution obtained in Examples 5A and 5B were measured as described above. The results are given in the following table:

Table IV

Solution	Transmission, per cent						
	White	Blue	Green	Red	Orange	Bluegreen	Violet
Example 5A	99	91	98	100	100	98	94
Example 5B	80	[1] 48	65	88	83	71	63

[1] When the polymer of Example 5B was heated to only 100° C., a blue light transmission of 51 per cent was observed.

From the above table it can be seen that the gaseous acid anhydrides (e. g. carbon dioxide) heretofore proposed in the prior art for the purpose of producing solutions of polymers of acrylonitrile of improved color properties do not provide improvements comparable to those obtainable according to our invention, even where the polymers are prepared in the manner described in our copending applications referred to above.

In a manner similar to that illustrated other acids or anhydrides selected from the group set forth above can be employed to advantage. Metaphosphoric, metaphosphorous, pyrophosphorous, hypophosphoric and pyrophosphoric acids can replace the orthophosphoric, orthophosphorous, etc. acids used above. The phosphorus pentoxide used above can be replaced with other oxides of phosphorus, i. e. compounds of the general formula

$$P_2O_x$$

wherein x is a positive integer from 3 to 5, can advantageously be used in our invention.

While our invention has been described in detail above with particular reference to N,N-dimethylformamide as the solvent for the polymers of acrylonitrile, it is to be understood that N,N-dimethylacetamide can likewise be used to advantage. In order to use N,N-dimethylacetamide according to the present invention, the polymers of acrylonitrile must be prepared in manner described in our copending applications Ser. No. 49,651, Ser. No. 49,652 or Ser. No. 49,653, all filed on even date herewith. As described fully in those applications, polymers of acrylonitrile prepared in a manner other than the therein described methods (i. e. polymerizing the acrylonitrile in the presence of a persulfate polymerization catalyst, a water-soluble, inorganic sulfur-containing catalyst activation and one of the specified acids) fail to give solutions of the polymers which are suitable for spinning into fibers.

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 advantageously be 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 following are pH measurements which were made on pure N,N-dimethylformamide, N,N-dimethylacet-

amide, and on mixtures of these solvents with various acids or anhydrides:

Solvent	pH
Pure DMF [1]	10–11
Pure DMA [2]	9.2–9.3
DMF [1]+2% H_3PO_4	3.5
DMF [1]+1% H_3PO_4	3.8
DMF [1]+2% P_2O_5	2.1–2.5

[1] N,N-dimethylformamide.
[2] N,N-dimethylacetamide.

The reduction in pH does have a beneficial effect on the polymer solutions in some instances, however, as has been pointed out above, not all acids (e. g. hydrohalogen acids) give improved polymer solutions.

From the foregoing description and examples, it can be seen that the objects of our invention have been accomplished, and the art is provided with a convenient means for producing substantially water-solutions of polymers of acrylonitrile, which can be spun into fibers, or cast into sheets or films.

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 polymer of acrylonitrile containing in the polymer molecule at least 80 per cent by weight of acrylonitrile, N,N-dimethylformamide, and from 0.1 to 5.0 per cent by weight, based on the weight of the N,N-dimethylformamide, of an inorganic phosphorus compound selected from the group consisting of oxygen acids of phosphorus and oxides of phosphorus.

2. A polymer of acrylonitrile containing in the polymer molecule at least 80 per cent by weight of acrylonitrile dissolved in N,N-dimethylformamide containing from 0.1 to 5.0 per cent by weight, based on the weight of the N,N-dimethylformamide, of an inorganic phosphorus compound selected from the group consisting of oxygen acids of phosphorus and oxides of phosphorus.

3. A polymer of acrylonitrile containing at least 80 per cent by weight of acrylonitrile in the polymer molecule dissolved in N,N-dimethylformamide containing from 0.1 to 5.0 per cent by weight based on the weight of the N,N-dimethylformamide, of phosphorus pentoxide.

4. A polymer of acrylonitrile containing at least 80 per cent by weight of acrylonitrile in the polymer molecule dissolved in N,N-dimethylformamide containing from 0.1 to 5.0 per cent by weight based on the weight of the N,N-dimethylformamide, of an oxygen acid of phosphorus.

5. A polymer of acrylonitrile containing at least 80 per cent by weight of acrylonitrile in the polymer molecule dissolved in N,N-dimethylformamide containing from 0.1 to 5.0 per cent by weight based on the weight of the N,N-dimethylformamide, of hypophosphorous acid.

6. A polymer of acrylonitrile containing at least 80 per cent by weight of acrylonitrile in the polymer molecule dissolved in N,N-dimethylformamide containing from 0.1 to 5.0 per cent by weight based on the weight of the N,N-dimethylformamide, of orthophosphoric acid.

7. A homopolymer of acrylonitrile dissolved in N,N-dimethylformamide containing from 0.1 to 5.0 per cent by weight, based on the weight of the N,N-dimethylformamide, of phosphorus pentoxide.

8. A homopolymer of acrylonitrile dissolved in N,N-dimethylformamide containing from 0.1 to 5.0 per cent by weight, based on the weight of the N,N-dimethylformamide, of an oxygen acid of phosphorus.

9. A homopolymer of acrylonitrile dissolved in N,N-dimethylformamide containing from 0.1 to 5.0 per cent by weight, based on the weight of the N,N-dimethylformamide, of hypophosphorous acid.

10. A homopolymer of acrylonitrile dissolved in N,N-dimethylformamide containing from 0.1 to 5.0 per cent by weight, based on the weight of the N,N-dimethylformamide, of orthophosphoric acid.

HARRY W. COOVER.
THEODORE E. STANIN.
JOSEPH B. DICKEY.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,404,728	Finzel	July 23, 1946