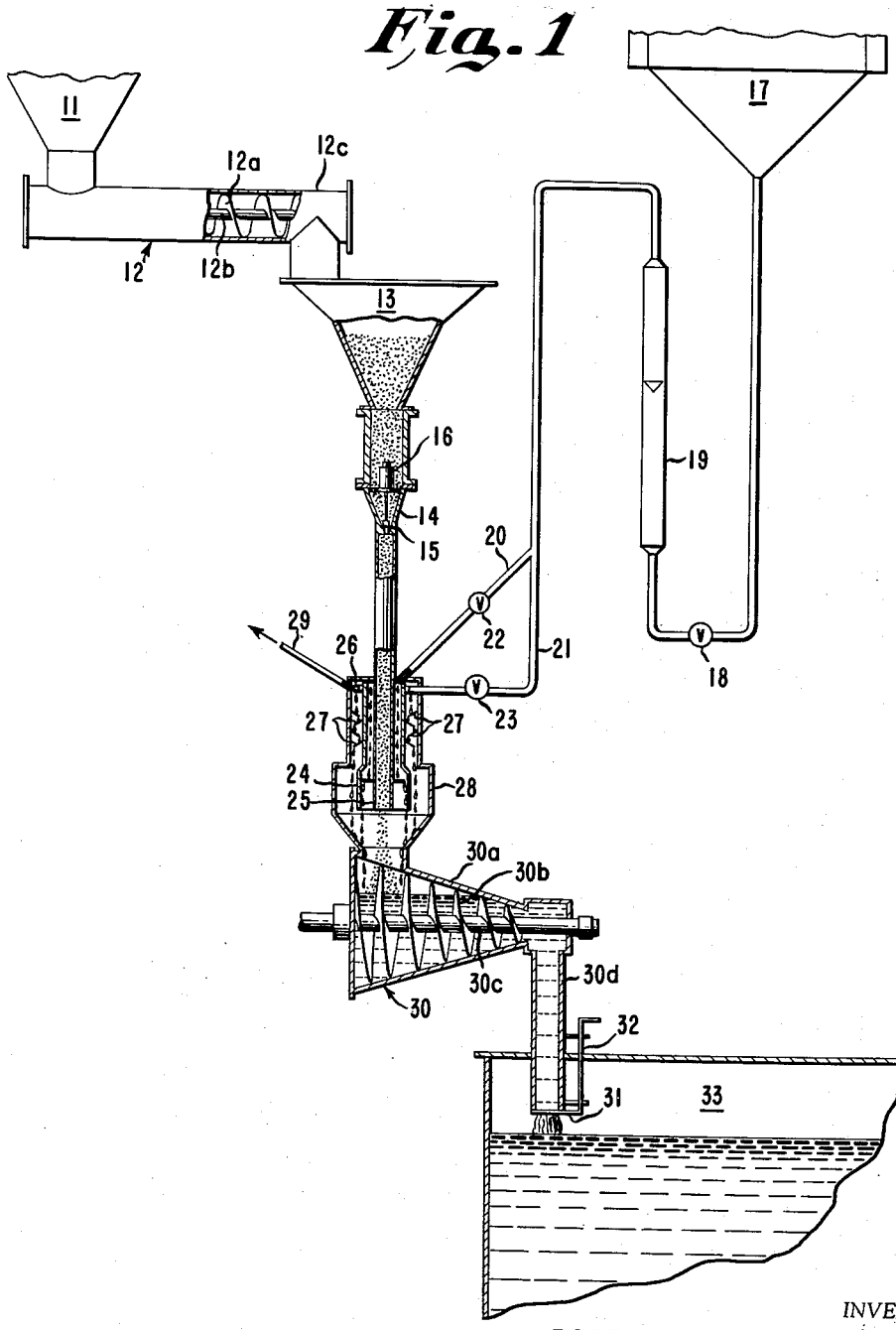
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PROCESS FOR CONTINUOUSLY DISSOLVING ACRYLONITRILE POLYMER AND SPINNING THE RESULTING SOLUTION

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Fig. 1



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PROCESS FOR CONTINUOUSLY DISSOLVING ACRYLONITRILE POLYMER AND SPINNING THE RESULTING SOLUTION

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This invention relates to the preparation of solutions of polymers of acrylonitrile, particularly solutions suitable for the preparation of shaped polymer articles such as fibers and films.

In the art of spinning fibers from acrylonitrile polymers, the quality of the spinning solution is important. Inhomogeneities in the solution not only limit the useful life of spinnerets and filtering devices, but also have a noticeable detrimental effect on fiber quality, no matter how efficient the filtration. The color of the solution is also important in that it is directly related to ultimate fiber color. For textile uses it is desirable that the fibers be as colorless as possible, both for use in the fabrication of white products, and for uses in which dyeing to pastel shades is desired.

It is an object of this invention to prepare acrylonitrile polymer solutions of good quality. It is a further object to prepare acrylonitrile polymer solutions of improved spinnability. It is yet another object to provide a continuous process for the preparation of acrylonitrile polymer solutions of good quality and low color. Other objects will appear hereinafter.

According to this invention acrylonitrile polymer in the form of small granules is introduced into a reduced pressure zone while a liquid, which is a solvent for the polymer, is simultaneously introduced to the same zone in such a manner as to envelop the entering polymer within two substantially cylindrical curtains of liquid; the polymer and solvent are mixed at a pressure of less than about 10 lbs./sq. in. abs., preferably less than about 7 lbs./sq. in. abs., and then the resulting solution is discharged from the reduced pressure zone. The solution may be utilized directly for spinning into fibers by conventional procedures.

FIGURE 1 depicts one arrangement in which the process of the invention may be carried out. In this drawing, **11** is a conical bin holding a supply of acrylonitrile polymer granules, open to the atmosphere, **12** is a screw metering device consisting of a screw flight **12***a* mounted on shaft **12***b*, said shaft being driven by means not shown, and said screw flight rotating inside closely fitting housing **12***c*. Metering screw **12** feeds polymer into the conical container **13**, tapering outlet **14** of which is fitted with conical plug **15**, movable in the vertical direction by pneumatic cylinder **16**. Solvent is supplied from jacketed vessel **17**, through valve **18** and rotameter **19** to lines **20** and **21** fitted with valves **22** and **23**, respectively. Solvent from line **20** passes through the annular space between cylinders **24** and **25**, and falls from the bottom edge of cylinder **24**. Solvent from line **21** flows through openings uniformly spaced about annular ring **26**, over baffles **27**, and thence through the annular space between cylinders **24** and **28**. Cylinder **28** is evacuated through pipe **29** by pump, not shown. Cylinder **28** is connected at the bottom to tapering screw mixer **30**, consisting of housing **30***a*, closely fitting screw flight **30***b* mounted on shaft **30***c* which is driven by motor not shown, and exit pipe **30***d*. Exit pipe **30***d* is fitted with closure device **31** mounted on rotatable rod **32**. Exit pipe **30***d* feeds into jacketed cylindrical vessel **33**, from which solution can be removed.

The process of this invention is useful for preparing solutions from any granulated solid material, but it is particularly useful for preparing solutions of acrylonitrile polymers including polyacrylonitrile, and preferably copolymers of acrylonitrile with other copolymerizable vinyl monomers in which the combined acrylonitrile content of the copolymer is at least about 85%. Mixtures of acrylonitrile polymers may likewise be used. Copolymers of acrylonitrile show advantages over acrylonitrile homopolymer in that a lower temperature may be used in the solvent heater without preventing complete dissolution of the polymer in the solvent in the screw type mixer.

The process of this invention is advantageous for use with solvents generally and, when applied to acrylonitrile polymers, may be utilized with any of the ordinary organic solvents for acrylonitrile polymers. Application of reduced pressure to both polymer and solvent just before mixing results in improvements in continuity in the preparation of yarns from the solutions. The continuous nature of this process and the economies it presents due to shortened holdup times at all stages of the solution preparation are advantages which accrue regardless of the solvent used. With this process there is no need for deaerating the polymer solution or to supply additional heating to completely dissolve the polymer as is customary in prior art practices. The invention is of particular advantage when dimethylformamide and dimethylacetamide are the solvents utilized because of the normal tendency of solutions in these solvents to develop color during heating. Even with these materials this invention provides substantially less colored solutions (more nearly water-white) than possible with prior art procedures for preparing polymer solutions. With either of these two common and efficient solvents the process results in solutions and hence fibers of improved color, improved solution processability, and improved processing economics.

The equipment shown in the drawing is advantageous for carrying out the invention, but those skilled in the art will readily see the possibility of using variations. Any sort of loss-of-weight system coupled with a screw feeder or continuous belt may be used to convey the polymer at a predetermined rate to the container above the evacuated mixer. In many instances it will be preferable to have two such systems feeding the same container so that one may be used to feed the mixer at the prescribed rate while the second is being refilled for use. The plug valve at the bottom of the container **13** may be replaced if desired with a substantially air-tight rotating feeder if one is available, but no rotary feeder has been found which is sufficiently air-tight to be suitable. The poppet valve shown has proved to be far superior to any known rotary type in actual practice.

Other means may be used for metering solvent into the apparatus. Loss-of-weight systems and positive displacement pumps may take the place of the rotameter shown. Any system which will feed the solvent in at a predetermined constant rate is acceptable.

The design of the scrubbing system in which the polymer and solvent are mixed is not critical, but the design shown has proven to be particularly effective. It provides for envelopment of the solid granules passing through vessel **28** within at least one cylindrical curtain of solvent and prevents the polymer and any entrained air from being carried out vacuum line **29** of the apparatus by a scrubbing system comprising cascading streams of falling solvent. In practice it has been found that no losses of polymer through the vacuum line are incurred.

Other mixers may be used in place of the tapering screw mixer shown in the drawing. However, this particular type of mixer is particularly efficient for the prep-

aration of viscous solutions of the type under consideration and it is preferred. This mixer operates efficiently under vacuum and readily builds up a positive pressure at its point of discharge. The type of valve used at this discharge point is not critical, but the valve shown is unusually suited for its purpose. The valve used should seal the discharge tube at the start of the operation and should readily be opened after the operation has commenced to allow the passage of the viscous solution which is the product of the process of the invention. It is particularly desirable to use a valve which can be opened or closed mechanically according to the pressure built up in the discharge pipe.

Rates of addition of polymer and solvent to the mixer will depend on the size of the particular mixer used and the rate of solution preparation desired. For greatest efficiency in terms of good solution quality, minimum residence time of the ingredients within the mixer itself should be about 5 seconds and preferably about 10 seconds. In order that the color of the resulting solution should be held at a minimum, residence time of the ingredients in the mixer should not exceed about 5 minutes and preferably should not exceed about 2 minutes. Residence time of the solution in vessel **33** is in no way critical to the solution process but for reasons of good color should be held to whatever minimum time is sufficient to maintain enough inventory to prevent loss of continuity in the spinning operation when the number of spinning positions is occasionally changed.

The particle size range of the polymer used in the process may vary from about 1 micron to about 1 millimeter diameter. It is preferred that the particle size is such that about 90% of the polymer will pass through a 100-mesh screen, 70% will pass through a 200-mesh screen, and about 20% will pass through a 325-mesh screen. The solvents used in the process should be preheated to a temperature of about 45° C. to about 90° C. and preferably to a temperature of about 65° C. to about 75° C.

The following example illustrates the invention. All parts and percentages are by weight unless otherwise indicated.

Example

This example illustrates preparation of a 29% solution in dimethylformamide of a copolymer composed of 94% combined acrylonitrile and 6% methyl acrylate and having an intrinsic viscosity of 1.50 as determined in dimethylformamide. Referring to FIGURE 1, a supply of this polymer is maintained in bin **11**. Vessel **17** is filled with dimethylformamide heated to 72° C., and this temperature is maintained throughout the run by passage of steam into the jacket of vessel **17**. Addition of more dimethylformamide to the vessel is made as desired. At the start of the run the plug **15** is allowed to drop into orifice **14**, thereby closing it, the rod **32** is rotated so that the closure device **31** entirely covers the bottom of pipe **30***d*. Valve **18** is also closed. The system bounded by these closures (vessel **28** and screw mixer **30**) is then evacuated by applying suction through pipe **29** by a vacuum pump not shown. When the vacuum inside the apparatus reaches a value of 12 inches of mercury, valve **18** is opened and adjusted to allow a flow rate of 13,000 lbs. of dimethylformamide per hour as measured on the calibrated rotameter **19**. Within 3 seconds, the metering screw **12** is put into operation to feed polymer to the vessel **13** at the rate of 5,300 lbs. per hour and pneumatic cylinder **16** is actuated to raise the plug **15** from the opening **14** to allow the polymer to flow through that opening into the cylinder **25**. The polymer used in this test is in the form of substantially spherical particles ranging from about 1 micron to about 1 millimeter in diameter. Because of the reduced pressure in vessel **28**, the polymer flows through opening **14** readily. Valves **22** and **23** are adjusted in advance so that approximately one fifth of the solvent passes through line **21** and the remainder through line **20**. After pneumatic cylinder **16** has been actuated, screw mixer **30** is put into operation. This mixer is 26 inches in diameter at its large end and 6 inches in diameter at its small end, 44 inches long, and the screw has a pitch of 10°. The screw is driven at a speed of 230 r.p.m. Polymer and solvent are admixed in this mixer, and the resulting solution is forced by the screw into pipe **30***d*, thereby building up a positive pressure. When this pressure reaches a value of 1.0 p.s.i.g., rod **32** is rotated to partially remove the closure device **31** and partially open pipe **30***d*. Solution of polymer is thereby allowed to issue into vessel **33**.

Addition of polymer and solvent is continued at the above rates. The position of plug **15** is adjusted to maintain the level of polymer in vessel **13** at a substantially constant height as seen through a sight glass not shown in the drawing. Valve **18** is adjusted as necessary to maintain constant solvent flow as shown by the rotameter **19**. Evacuation of the equipment is continued past the 12-inch level mentioned above, and is maintained at 25 inches of mercury. The position of the closure **31** is adjusted to maintain a pressure of 1 p.s.i.g. in the line **30***d*.

Polymer solution in vessel **33** is maintained at 64–68° C. by a flow of hot water through the jacket of that vessel. A mixture of 85% nitrogen and 15% carbon dioxide is passed through vessel **33** above the level of the solution at a rate of 3 cubic feet per minute. Polymer solution is pumped from this vessel as desired and used for the preparation of fibers. Average residence time of solution in vessel **33** at this relatively low temperature is about 7 hours.

Samples of polymer solution taken from vessel **33** have a viscosity of 100 poises as measured at 125° C. Other samples of the solution, heated to 100° C. for four hours and then diluted with dimethylformamide to a concentration of 5.8% polymer, are measured for optical density at 400 millimicrons against a sample of pure dimethylformamide using a Beckman model DU spectrophotometer. The optical density thus measured, when multiplied by 100, is taken as the heated color value (HCV) of the solution. The solution has an average HCV of 20. By comparison, solutions prepared in much the same way except that the mixer is not evacuated and the ingredients were not subjected to vacuum during mixing have an average HCV of 22.

In carrying out the process of this invention the ratio of solids to solvent added to the mixing vessel may be regulated to provide solutions containing from about 20% to about 40% solids by weight. For the preparation of acrylonitrile polymer solutions suitable for spinning into fibers the solids-solvent ratio is preferably regulated to provide acrylonitrile polymer solutions containing between about 28% and about 32% solids by weight. Solids and solvent should be added to the mixing vessel at a rate sufficient to maintain a level of mixture in screw mixer **30** preferably at a point about two-thirds the height of the mixer at its deepest end, although the level may fall to the top of the smaller end of the mixer or may rise to the top of the deep end of the mixer without adverse affect. Preferably, the level of mixture will not be allowed to rise into tank **28**, this tank being reserved for free fall of solvent and solids. Solids utilized in the process should be sufficiently dry to facilitate transmission into the mixing vessel and normally solids which are dry to the touch are sufficiently dry for this purpose.

I claim:

1. A process which comprises continuously passing acrylonitrile polymer, selected from the group consisting of homopolymers of acrylonitrile and copolymers of acrylonitrile with unsaturated monomers copolymerizable therewith wherein the copolymers contain at least about 85% combined acrylonitrile by weight, in the form of substantially dry, small granules into a zone of reduced pressure, simultaneously introducing into the same zone two streams of a liquid, selected from the group con-

sisting of dimethylformamide and dimethylacetamide, in the form of two separated concentric cylindrical curtains of liquid about the entering acrylonitrile polymer, said zone being maintained at a reduced pressure of less than about 10 lbs./sq. in. abs., admixing the solvent and acrylonitrile polymer in the reduced pressure zone until solution is effected, continuously discharging the said solution from the reduced pressure zone and spinning said solution, as soon as formed and without recirculation, at superatmospheric pressure into fibers, residence time of the liquid and acrylonitrile polymer in the reduced pressure zone being between about 5 seconds and about 5 minutes.

2. The process of claim 1 in which the residence time is between about 5 seconds and about 2 minutes and the temperature within the reduced pressure zone is between about 60° C. and about 75° C.

3. The process of claim 1 in which the granules of acrylonitrile polymer are within the particle size range from about 1 micron to about 1 millimeter in diameter.

4. The process of claim 3 in which the acrylonitrile polymer is a copolymer containing about 94% combined acrylonitrile and about 6% methyl acrylate by weight.

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