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SPINNING OF CELLULOSE ACETATE GUM

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17 Claims. (Cl. 18—54)

This invention relates to the wet method of forming filaments, ribbons and films from artificial plastic material dissolved in acid solutions. More particularly it relates to the wet spinning of cellulose acetate gums, i. e. acetic acid solutions of cellulose acetate, and to coagulating baths therefor.

Wet spinning of organic derivatives of cellulose and the like, particularly of cellulose acetate, offers many obvious advantages over the evaporative or dry method of spinning, principally in the matter of economy of operation through elimination of process steps involved in the preparation of the derivative for dry spinning, and through elimination of expensive solvent loss and the need for solvent recovery steps. Advantages less obvious are, (1) production of many more filaments per spinning position than is now possible by the dry spinning process, and (2) the ease with which stretch spinning technique is combined with wet spinning, whereby to improve the physical properties of the product. With these advantages in mind, the art has for a number of years striven to perfect a commercially feasible method of wet spinning cellulose acetate, and like derivatives. However, efforts to wet spin such materials directly from the gum stage, i. e. from their solution in acid, have met with such little success that the present trend is to isolate the filament-forming material, and to dissolve it in an organic solvent to form a spinning solution, as in the dry spinning process, and extrude the solution so formed into a coagulating bath. Obviously many of the economies inherent in true gum spinning are thus lost. Of the disclosures which do relate to true gum spinning, most are restricted to the extrusion of primary or chloroform-soluble acetate, i. e. acetate containing 59% to 62% of combined acetic acid. The coagulating baths involved in these disclosed methods do not permit of a satisfactory filament when secondary or acetone-soluble cellulose acetate is made the basis of the spinning solution, and the practical inoperativeness of the secondary acetate is indicated. However, filaments made of primary cellulose acetate are inferior to those made of secondary acetate because:

1. They are less stable to hydrolysis.
2. They cannot be dyed satisfactorily with existing dyes.
3. They are inherently more brittle than yarn spun from a secondary or acetone-soluble cellulose acetate.

Thus, known methods for wet spinning cellulose acetate and like filament-forming materials, from their solution in acids, are of seriously limited application due primarily to the lack of a suitable coagulating bath.

It is, therefore, an object of this invention to provide a new and improved coagulating bath for the wet spinning or casting of cellulose acetate gum and other filament- or film-forming materials in acid solution. A further object of the invention is to provide an improved wet spinning process for coagulable filament-forming materials in an acid solution. Still a further object of this invention is to provide an improved stretching process which may be carried out simultaneously with the wet spinning process. Other objects will be apparent from the description that follows.

These objects are realized by my invention which comprises coagulating extruded structures of water-insoluble materials coagulable from acid solutions by extruding the same into an aqueous bath of a water-soluble amine having an ionization constant higher than 1×10^{-6}. Representative amines falling in this classification and well suited as coagulants in accordance with my invention are triethanolamine, diethanolamine, monoethanolamine, benzylamine, butyl amine, ethylenediamine, propylene diamine, hexamethylene diamine, morpholine, hydrazine, tetraethylene pentamine, triethylene tetramine, diethylene triamine, and hydroxyethyl ethylene diamine.

Coagulation of the coagulable filament-forming material by a suitable amine bath is, to a large extent, the result of a chemical reaction between the amine and the acid, resulting in the formation of a salt. For instance, the reaction between diethanolamine and acetic acid is as follows:

$$(OHC_2H_4)_2NH + CH_3COOH \rightarrow (OHC_2H_4)_2NH.CH_3COOH$$

By heating the spent coagulating bath containing the amine acid salt, usually in the presence of water, the above reaction is reversed and the acetic acid, due to its higher vapor pressure, is distilled from the solution and may thus be recovered and the free amine base returned to the coagulating bath for reuse.

The particular amine chosen as a coagulant may depend on whether the amine acid salt is to be regenerated to recover the free acid and free base for reuse or whether the amine acid is to be discarded. In general, for ease in recovery of the amine, it should have, preferably, a boiling point greater than the temperature of

the regeneration. For instance, in the spinning of cellulose acetate from acetic acid solutions in triethanolamne coagulating bath, the regeneration of the triethanolamine from triethanolamine acetate is preferably carried out at a temperature of about 160° C. to 180° C. which is substantially below the boiling point of the triethanolamine (280° C.). Furthermore, if the amine is to be recovered for reuse, the tertiary amines are preferred to the primary or secondary amines because the latter amines tend to form amides during regeneration according to the following reaction:

$$(OHC_2H_4)_2NH.CH_3COOH \xrightarrow{\text{Heat}} (OHC_2H_4)_2NCOCH_3+H_2O$$

The application of my invention to the wet spinning of cellulose acetate gum is illustrated by the following general procedure.

Cellulose acetate gum prepared by the esterification of cellulose and hydrolyzed to obtain the desired percentage of combined acetic acid is treated with a salt of acetic acid, for example, sodium acetate, to neutralize or render ineffective the sulfuric acid or other acid catalyst used to effect esterification and hydrolysis and thereby arrest further hydrolysis. The cellulose acetate gum is filtered to remove any undissolved material and stored in suitable tanks for a sufficient length of time to allow the air entrained therein to cream out. The gum, now ready for spinning, is fed to the spinneret and extruded into the aqueous amine bath to form filaments of gel cellulose acetate. After several inches of bath travel, the group of filaments is passed around one or more suitable bath guides and finally withdrawn from the coagulating bath by means of one or more positively driven rolls. The gel yarn may be collected on a bobbin, in a centrifugal spinning bucket, in a stationary or slowly revolving can, on a suitable conveyor belt, or the gel yarn may be cut at this point into staple lengths and further processed on a conveyor belt or on other suitable means.

If it is desired to stretch the yarn after leaving the coagulating bath in order to obtain a higher tenacity, the yarn may be led to a second set of rolls, the speed of which is regulated with respect to the first set of rolls in order to obtain the desired degree of stretch. The yarn may be stretched in air or, where a higher degree of stretch is desired, the yarn may be passed through a tank containing acetic acid and water at a controlled temperature and then stretched.

The yarn after spinning and/or stretching may be washed in the form collected or withdrawn from the takeup package and washed on-the-run in a counter-current washing system. In either case, the acetic acid-amine acid salt wash water effluent may be sent to regeneration equipment. In regenerating amine, it is generally desirable to first evaporate the major portion of the water of dilution under reduced pressure so as to obtain a stronger acid distillate which is subsequently steam distilled at a suitable temperature. (Preferably 80% to 85% of the water of dilution is evaporated to give an acid distillate of about 20% whereas if the water solution is not at all reduced, the acid concentration of the acid distillate would be approximately 10% to 12%). At this point, splitting of the amine acid salt takes place and the amine and acid may be separated and recovered.

The aqueous amine coagulating bath is circulated through a heat exchanger to maintain the desired temperature and may be introduced into the spinning trough so that the flow is either concurrent or counter-current to the direction of travel of the yarn. The volume of flow is controlled so that there is not an excessive increase in acid or amine acid salt near the face of the spinneret. The coagulating bath is bucked up from time to time with an aqueous solution of the desired amine and continuously, or intermittently from time to time, a portion of the bath is removed for regeneration of the free base and free acid.

In a preferred embodiment of this invention, a filtered deaerated cellulose acetate gum containing 14% to 15% cellulose acetate (54.5% to 57.7% combined acetic acid), 5% to 10% water, and a small percentage of sodium sulfate, the balance being acetic acid, is transferred by mechanical means to a metering pump and after a final filtration is spun through a suitable spinneret into a coagulating bath of 12% triethanolamine, 20% triethanolamine-acetate, in water at 9° C. The length of bath travel will depend on the denier of the yarn being spun and the spinning speed. The bath travel should be made as short as possible consistent with good spinning so as to reduce to a minimum the amount of amine acid salt formed in the coagulating bath. The gel yarn may be collected on any suitable collecting device or, if desired, the yarn may be subjected to a stretching treatment prior to collection.

My invention is further illustrated by the following examples, wherein percentages are percentages by weight.

Example I

Cellulose acetate gum containing 14% cellulose acetate (54.5% combined acetic acid), 4% water, 82% acetic acid, was spun through a 200-hole spinneret into the following coagulating baths of diethanolamine in water (containing substantially no diethanolamine acetate or other salt) at 23° C. The yarn was stretched 25% in air, collected in the form of loose coils in a perforated can, washed and dried free of tension.

Run	Conc. of diethanolamine in water	Final wind-up speed	Denier	Dry tenacity G. P. D.	Dry elongation
	Per cent	*In./min.*			*Per cent*
A	45	2000	1367	.76	58.0
B	30	2300	1413	.85	50.2
C	15	2760	1231	.91	28.2

Example II

Cellulose acetate gum containing 14% cellulose acetate (54.5% combined acetic acid), 4% water, 82% acetic acid, was spun into the following baths containing triethanolamine and triethanolamine-acetate. The yarn was collected on bobbins, washed, and dried.

Run	Triethanolamine	Triethanolamine acetate	Water	Coag. bath temp.	Denier	Dry tenacity G.P.D.	Dry elongation
	Per cent	*Per cent*	*Per cent*	*°C.*			*Per cent*
D	5	20	75	18	1160	.94	22.9
E	10	20	70	19.5	1134	1.01	23.6
F	10	30	60	20	1011	.88	12.3
G	5	30	65	21	1130	.65	14.8
H	5	20	75	9	1124	1.09	23.9
I	5	30	65	11.5	1106	1.05	26.2

Example III

Gum containing 15% cellulose acetate (54.5% combined acetic acid), 5% water, 80% acetic acid, was spun through a 40-hole spinneret, hole diameter 0.003 inch, into the following amine coagulating baths substantially free of the amine acetate or other salt. The yarn was collected on bobbins, washed, and dried.

Run	Amine in water	Coag. bath temp.	Denier	Dry tenacity G. P. D.	Dry elongation
	Per cent	*°C.*			*Per cent*
J. Benzylamine	25	10	325	1.16	12.6
K. Ethylenediamine	25	10	324	1.15	19.8
L. Hexamethylene diamine	25	10	364	1.00	26.0
M. Morpholine	25	10	468	1.03	16.1

Example IV

Cellulose acetate gum containing 14.16% cellulose acetate (54.5% combined acetic acid), 2.94% water, 82.90% acetic acid, was spun through a 200-hole spinneret, hole diameter 0.0025 inch, into a 50% diethanolamine bath in water at 28° C. and substantially free of diethanolamine-acetate. After coagulation, the yarn was run through a 30% acetic acid-water bath at 24° C. and stretched the following amounts. The yarn was washed and dried free of tension.

Run	Stretch	Dry tenacity G. P. D.	Dry elongation
	Per cent		*Per cent*
N	0	.87	45.5
O	25	1.22	17.0
P	50	1.71	11.0
Q	75	1.87	6.4

It is understood, of course, that the above examples are for purposes of illustration only and that the invention is not limited to the exact conditions therein recited but is susceptible rather to wide variations as indicated hereinafter.

The temperature of the coagulating bath depends to some extent upon the composition of the coagulating bath. For most purposes, best results are obtained at temperatures below about 30° C. and more specifically in a temperature range of from about 8° C. to about 11° C.

The combined acetic acid content of the cellulose acetate may vary quite widely as, for instance, from 50% to 62%, although for satisfactory dyeing and optimum physical properties a cellulose acetate having from 54.5% to 57.7% combined acetic acid is preferred.

The concentration of the amine in water may vary quite widely, but in general the best results are obtained when the concentration of the amine, both free and combined, is not over 50% of the total weight of the coagulating bath.

Although I have described my invention primarily in terms of wet spinning cellulose acetate dissolved in acetic acid, the invention is generally applicable to the spinning or casting of any filament or sheet-forming material in acid solution, which material is water-insoluble and coagulable in the amine water bath. Other cellulose esters may be cast or spun, for instance, a solution of cellulose propionate in propionic acid, or a solution of a mixed ester such as cellulose acetate propionate or cellulose acetate butyrate in a suitable aliphatic carboxylic acid. Polyvinyl acetate in acetic acid, and acetals such as polyvinyl butyral or polyvinyl formal in acetic acid, or other suitable acid solvent, may be formed into products in accordance with this invention. Nylon when dissolved, for instance, in a formic acid solution, is also coagulable by the amine baths of this invention to produce fibers, filaments, film, and the like

I claim:

1. In the process of forming filaments, ribbons, and films of artificial plastic material wherein an acid solution of said material is extruded into a coagulating bath, the step which comprises extruding said solution into a coagulating bath comprising essentially an aqueous solution of a water-soluble amine having an ionization constant greater than 1×10^{-6}.

2. A process according to claim 1 wherein the amine is a water-soluble tertiary amine.

3. In the process of spinning filaments of artificial filament-forming material wherein an acid solution of the material is spun in a coagulating bath, the step which comprises spinning said solution in a bath comprising essentially an aqueous solution of a water-soluble amine having an ionization constant greater than 1×10^{-6}.

4. A process according to claim 3 wherein the amine is a water-soluble tertiary amine.

5. In the process of spinning filaments of filament-forming organic derivatives of cellulose wherein an acid solution of said derivative is spun in a coagulating bath, the step which comprises spinning said acid solution in a coagulating bath comprising essentially an aqueous solution of an amine whose ionization constant is greater than 1×10^{-6}.

6. A process according to claim 5 wherein the amine is a water-soluble tertiary amine.

7. In the process of spinning filaments of cellulose acetate wherein a solution of cellulose acetate in acid is spun in a coagulating bath, the step which comprises spinning said solution in a coagulating bath comprising essentially an aqueous solution of an amine whose ionization constant is greater than 1×10^{-6}.

8. A process according to claim 7 wherein the amine is a water-soluble tertiary amine.

9. In the process of spinning filaments of cellulose acetate wherein a solution of cellulose acetate in acetic acid is spun in a coagulating bath, the step which comprises spinning said solution in a coagulating bath comprising essentially an aqueous solution of an amine whose ionization constant is greater than 1×10^{-6}.

10. A process according to claim 9 wherein the amine is a water-soluble tertiary amine.

11. The process which comprises spinning an acid solution of cellulose acetate, having from about 54.5% to about 57.7% by weight of combined acetic acid, in a coagulating bath comprising an aqueous solution of a water-soluble amine having an ionization constant greater than 1×10^{-6}.

12. The process which comprises spinning an acetic acid solution of cellulose acetate having from about 54.5% to about 57.7% by weight of combined acetic acid, in a coagulating bath comprising essentially an aqueous solution of an amine whose ionization constant is greater than 1×10^{-6}, while maintaining the temperature of said bath below about 30. C., and thereafter stretching and washing the formed filament.

13. The process which comprises spinning an acetic acid solution of secondary or acetone-soluble cellulose acetate in a spin bath consisting of

an aqueous solution containing not over 50% by weight, based on the total weight of the bath, of free and combined water-soluble amine having an ionization constant greater than 1×10^{-6}, while maintaining the temperature of the bath below about 30° C., and thereafter stretching and washing the formed filament.

14. The process which comprises spinning an acetic acid solution of secondary or acetone-soluble cellulose acetate in a spin bath consisting of an aqueous solution containing not over 50% by weight, based on the total weight of the bath, of free and combined water-soluble amine having an ionization constant greater than 1×10^{-6}, while maintaining the temperature of the bath within the range of from about 8° C. to about 11° C., and thereafter stretching and washing the formed filament.

15. The process which comprises extruding a cellulose acetate gum containing from 14% to 15% by weight of cellulose acetate having from 54.5% to 57.7% by weight of combined acetic acid, 5% to 10% by weight of water, a small amount of sodium sulfate, and the balance being acetic acid, through a spinneret into a coagulating or spin bath consisting of an aqueous solution containing about 12% by weight of triethanolamine and about 20% by weight of triethanolamine-acetate, while maintaining the temperature of said bath at about 9° C.

16. A coagulating or spin bath especially suitable for the wet spinning of secondary cellulose acetate which comprises essentially not more than 50% by weight, based on the total weight of the bath, of free and combined water-soluble amine having an ionization constant greater than 1×10^{-6}, the remainder of the bath being water.

17. A coagulating or spin bath especially suitable for the wet spinning of secondary cellulose acetate which consists of an aqueous solution containing about 12% by weight of triethanolamine, about 20% by weight of triethanolamine-acetate, and about 68% by weight of water.

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CERTIFICATE OF CORRECTION.

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It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 2, first column, line 3, for "triethanolamne" read --triethanolamine--; line 8, for "(280° C.)" read --(208° C.)--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 23rd day of February, A. D. 1943.

Henry Van Arsdale,

(Seal) Acting Commissioner of Patents.