United States Patent Office 3,007,764 Patented Nov. 7, 1961

3,007,764

PROCESS OF PREPARING VISCOSE RAYON

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No Drawing. Filed Oct. 1, 1957, Ser. No. 687,355
7 Claims. (Cl. 18—54)

The present invention relates to a novel and useful process for the production of regenerated cellulose structures. More specifically it relates to an improvement in the conventional process for the preparation of regenerated cellulose shaped structures such as filaments, fibers, ribbons and the like, by extruding viscose into an aqueous acidic spinning bath.

It is known that the addition of certan low-molecular weight aldehydes, preferably formaldehyde, to the acid spinning baths used in the coagulation and regeneration of filaments by the viscose process leads to an increase in the stretch which may be imposed on the filaments during spinning and, hence, to an improvement in the strength of the ultimate product. A process of this type, employing formaldehyde, is described in U.S.P. 2,452,-130, issued to G. M. A. Kayser on October 26, 1948.

Although the use of formaldehyde in the spinning bath is very desirable from the standpoint of improvements in the quality of the regenerated cellulose product obtained, serious difficulties are encountered when the spinning is continued for long periods of time as must be done in the commercial practice of the process. After some hours of spinning a hard crystalline material begins to precipitate in the bath. These hard crystalline deposits are not to be confused with sludge formation due to metal sulfides, metal trithiocarbonates, free sulfur, etc., which occurs in most viscose spinning baths. These sludges cause some difficulty but may be dealt with by known methods. The hard crystalline material which deposits from the formaldehyde-acid spinning bath, forms on the wall of the bath lines and on other equipment whenever the bath comes in contact with it. With continued spinning these hardened deposits build up and clog the bath lines and are very difficult, and sometimes almost impossible, to remove. Thus, processes of this type are commercially unattractive unless some means of alleviating this condition can be found.

It is an object of the present invention therefore to produce regenerated cellulose structures. Another object is the production of regenerated cellulose structures by an improved process. A still further object is the production of regenerated cellulose structures whereby crystalline deposits in the spinning bath are prevented. Other objects will become apparent hereinafter from the descriptions, the examples and the claims.

Thesse objects are accomplished by the present invention which provides an improvement in the process of producing a shaped structure of regenerated cellulose by extruding viscose into a formaldehyde-containing acid bath, the improvement which comprises extruding the viscose in the presence of a nitrogen derivative selected from the group consisting of the ammonium ion, a primary alkyl amine containing up to eight carbon atoms, formamide, N-methyl formamide, acetamide, N-methyl acetamide, N,N-dimethyl acetamide, N,N'-dimethyl urea and 3,3-dimethyl hydantoin. By the term "in the presence of" is meant that the nitrogen derivative is dissolved in the viscose and/or the acid bath. The term "ammonium ion" signifies the radical $(NH_4)^+$. The term "primary alkyl amine" is used to designate a wholly aliphatic non-cyclic amine containing at least one $—NH_2$ group and only carbon, hydrogen, and nitrogen in the molecule.

While no limitation is intended as to any theory concerning the process of this invention, it has been found that the crystalline deposit consists primarily of trithiane. Apparently, the carbon disulfide and sodium hydroxide react so as to form sodium trithiocarbonate and some sodium sulfide. These compounds then react with the sulfuric acid in the spinning bath to form hydrogen sulfide and trithiocarbonic acid, and the trithiocarbonic acid decomposes to form hydrogen sulfide and carbon disulfide. Since it is known that hydrogen sulfide and formaldehyde react in acid solution to form hydroxy methyl mercaptan, it is believed that this then condenses to form trithiane. It is also believed that the trithiocarbonic acid reacts with formaldehyde to form bis-methylol trithiocarbonate which then decomposes to form the trithiane precursor hydroxy methyl mercaptan. The trithiane which is formed then precipitates out so as to form crystalline deposits. While these reactions appear to be the principal reactions in the formation of the crystalline deposit, other reactions may likewise take place so as to add to these deposits. In any event, the addition of the nitrogen derivative of the present invention in some way prevents such crystalline deposits from being formed as shown by the following examples. These examples are cited to illustrate the invention and are not intended to limit it in any manner.

EXAMPLE 1

Viscose containing 5.0% recoverable cellulose, 6.5% total alkali, calculated as NaOH, is prepared in the conventional manner using 60% carbon disulfide based on the weight of air dry cellulose pulp. This viscose is extruded into a spinning bath containing 10% sulfuric acid, 17.5% sodium sulfate, 9.5% zinc sulfate and 0.7% formaldehyde, the temperature of the bath being 55° C. The yarn is led through the bath for a distance of 40 inches, then stretched 165% in a dilute acid, secondary bath at a temperature of 94° C. When the amount of stretch imposed on the yarn in the secondary bath is increased to a level of 210%, the yarn breaks. The tenacity of the yarn after purification and drying is 4.85 g.p.d. A precipitate (principally trithiane) is observed to form in the bath within 24 hours. The test is repeated with 2.0% acetamide added to the bath. The spinning stretch is 170%, the breaking stretch 212% and no trithiane precipitate is observed. The yarn tenacity is 4.87 g.p.d. When no formaldehyde is used the breaking stretch is reduced to 146% and continuous spinning is impossible at 117% stretch.

EXAMPLE 2

This example illustrates the use of a compound which dissociates to form formaldehyde and an ammonia derivative, acetamide, when added to the spinning bath. Example 1 is repeated except that 3.0% N-methylol acetamide, formed by refluxing one mole of acetamide with one mole of para-formaldehyde at 150° C. for one hour, is added to the spinning bath. The breaking stretch of the yarn is 210% and no trithiane precipitate is observed. When nitrogen is bubbled through a sample of the bath at a temperature of 55° C., a substantial amount of formaldehyde is detected in the gas indicating dissociation of the acetamide derivative into acetamide and formaldehyde.

EXAMPLES 3 TO 36

In the following examples the composition of the spinning bath during extrusion is duplicated in order to test the effectiveness of various compounds. This is done by preparing a solution containing sodium trithiocarbonate and sodium sulfide in approximately the same concentrations as found in viscose, i.e., 0.61% sodium trithiocarbonate and 0.19% sodium sulfide. The sodium trithiocarbonate solution is prepared following the gen-

eral procedure described by Weeldenburg, Rec. Tran. Chim. 47, 496 (1928). An excess of carbon disulfide is added to a 2.5 normal sodium hydroxide solution and the mixture stirred for 24 hours at room temperature. The excess carbon disulfide is removed by bubbling nitrogen through the solution and the solution, which contains 5.7% sodium trithiocarbonate, diluted with water to give a concentration of 0.61%. Sodium sulfide was added to the solution to give a concentration of 0.19% of this compound. Fifty gram portions of this solution are added to 910 gram samples of spinning bath containing 10.0% sulfuric acid, 17.5% sodium sulfate, 9.5% zinc sulfate and 0.75% formaldehyde, the temperature being 55° C. One of these sample contains no additive. The others contain one of the compounds of this invention in a molar concentration equal to the molar concentration of formaldehyde. The samples are held at 55° C. for a total of 24 hours. Table 1 below shows the compounds used and the results obtained. For comparison, results obtained with a number of compounds not within the scope of this invention are shown.

Table 1

Example	Compound Added	Results
3	None	Trithiane precipitate.
4	Methylamine	No trithiane precipitate.
5	Ethylamine	Do.
6	Amylamine	Do.
7	Isoamylamine	Do.
8	Diethylaminopropylamine	Do.
9	Dipropylene triamine	Do.
10	Heptylamine	Do.
11	2-Methyl heptylamine	Do.
12	Dibutylamine	Trithiane precipitate.
13	Diethanolamine	Do.
14	Triethylamine	Do.
15	Diethyl hexylamine	Do.
16	N-Butyl diethanolamine	Do.
17	Cyclohexylamine	Do.
18	Aniline	Do.
19	Benzyltrimethyl ammonium hydroxide.	Do.
20	Dodecylamine	Insoluble in bath.
21	Formamide	No trithiane precipitate.
22	N-Methyl formamide	Do.
23	Acetamide	Do.
24	N-Methyl acetamide	Do.
25	N,N-Dimethyl acetamide	Do.
26	Chloroacetamide	Do.
27	N-Ethyl acetamide	Do.
28	Butyramide	Do.
29	N,N'-Dimethyl urea	Do.
30	N,N-Dimethyl formamide	Heavy trithiane precipitate.
31	Adipamide	Do.
32	Benzamide	Do.
33	Stearamide	Do.
34	Urea	Do.
35	Dithiooxamide	Do.
36	3,3-dimethyl hydantoin	No trithiane precipitate.

EXAMPLE 37

The procedure of Example 3 is repeated except that ammonium sulfate, in concentrations of 2 to 15% is added to the bath. With the higher concentrations it is necessary to reduce the concentration of sodium sulfate and zinc sulfate to dissolve all of the ammonium sulfate. In all cases where the molar concentration of ammonium sulfate is equal to or greater than the molar concentrations of formaldehyde, the crystalline trithiane precipitate is prevented. When no ammonium sulfate is added, a trithiane precipitate in considerable quantity is observed within 24 hours.

The foregoing examples show the effectiveness of the compounds of this invention in preventing the formation of trithiane in formaldehyde containing, acidic solutions which are exposed to the action of hydrogen sulfide and/or trithiocarbonic acid. By the use of these compounds in the viscose process, improved properties, due to the higher stretch made possible by the use of formaldehyde, are obtained without the highly undesirable formation of hard crystalline deposits of trithiane.

Any of the viscose rayon spinning baths which are common to the industry may be used in conjunction with the present invention. Such baths usually contain 4 to 12% sulfuric acid, 5 to 25% sodium sulfate, and may also contain various other materials such as magnesium sulfate, zinc sulftae, iron sulfate, glucose, etc.

The compounds which are effective in the process of this invention are nitrogen derivatives. Quite obviously, gaseous ammonia may be either directly absorbed in the acidic solution to form the derivative or may be absorbed in water to form ammonium hydroxide which may be added to the acidic solution. These compounds, therefore, may be added directly to the bath or formed in situ by the addition of reactants. In addition, the compounds may be added either to the viscose or to both the viscose and the spinning bath. In the preferred embodiment of this invention the ammonium derivative is added directly to the acid spinning bath.

The amounts of the nitrogen derivative which are employed in the present invention is not at all critical since the addition of a minor amount of the nitrogen derivative prevents minor amounts of the crystalline deposits from being formed. It has been found, however, that when the molar amount of the nitrogen derivative is approximately equal to or more than the molar amount of formaldehyde used in the bath, the crystalline deposits are substantially eliminated even upon prolonged use. For practical purposes, equi-molar amounts of formaldehyde and the nitrogen derivative are employed in the bath.

The compound which may be used to form the ammonium ion in solution is any compound which releases this ion under the conditions of extrusion. The preferred compound for forming the ammonium ion is ammonium sulfate since it is low in cost and is generally compatible with the viscose spinning system. However, effective results are also obtained with other soluble ammonium salts such as ammonium chloride, ammonium acetate, and the like.

The amines which are effective in the process of this invention are alkyl primary amines having up to 8 carbon atoms. Alkyl amines having substantially more than 8 carbon atoms are not sufficiently soluble in the bath to give effective results. Secondary and tertiary aliphatic amines, aromatic amines and cyclic amines are generally ineffective. As shown in the foregoing examples, amides other than those specifically shown to be effective are ineffective in producing the results of this invention.

Many other equivalent modifications will be apparent to those skilled in the art from a reading of the foregoing without departure from the inventive concept.

What is claimed is:

1. In the process of producing a shaped structure of regenerated cellulose by extruding viscose into a formaldehyde-containing, 4 to 12% sulfuric acid bath containing 5 to 25% sodium sulfate, the improvement which comprises extruding the viscose in the presence of a nitrogen derivative to prevent the formation of hard crystalline deposits consisting primarily of trithiane, said nitrogen derivative being selected from the group consisting of ammonium sulfate, formamide, N-methyl formamide, acetamide, N-methyl acetamide, N,N-dimethyl acetamide, N,N'-dimethyl urea and 3,3-dimethyl hydantoin, the maximum amount of formaldehyde in the bath being a molar amount approximately equal to the molar amount of said nitrogen derivative.

2. The process of claim 1 wherein the nitrogen derivative is present in an amount of about 2 to 3% by weight of the bath.

3. The process of claim 1 wherein the nitrogen derivative is ammonium sulfate.

4. The process of claim 1 wherein the nitrogen derivative is acetamide.

5. The process of claim 1 wherein the nitrogen derivative is formamide.

6. The process of claim 1 wherein the nitrogen derivative is N-methyl formamide.

7. The process of claim 1 wherein the nitrogen derivative is N-methyl acetamide.

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