

UNITED STATES PATENT OFFICE

2,593,466

VISCOSE SPINNING SOLUTION

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No Drawing. Application July 16, 1948,
Serial No. 39,194

13 Claims. (Cl. 106—165)

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The present invention has for its object a new and improved viscose solution for use in the production of such yarn as well as a process by which such viscose solutions and yarn may be produced.

In the preparation of viscose spinning solutions the viscose is customarily filtered one or more times through various fine cloth media before it is extruded into a coagulating bath. Difficulty however is frequently encountered in producing viscose solutions that are free of minute undispersed and undissolved particles which clog the pores of the filter media prematurely or pass through the pores and later clog the orifices of spinnerets thereby resulting in yarns of low strength and poor uniformity. Such extraneous particles may consist of resinous materials found in wood pulp undissolved or partially dissolved cellulose xanthate gels and semisolids, etc. The presence of such particles in a filtered viscose solution is usually evidenced by the lack of transparency and high turbidity of the spinning solution. In some situations even relatively large sized particles in the form of fluid semisolids or gel-like substances successively slip through the pores of the filter media. In addition such particles upon standing in a stored and filtered viscose solution may tend to agglomerate and as a result further increase the difficulties mentioned.

In order to eliminate one or more of the difficulties mentioned there have been proposed heretofore the incorporation of various organic surface-active compounds at one or more of the stages of viscose production. In general however such additives have not been entirely successful for one or more of the following reasons, i. e., they may be unstable in the caustic soda solutions encountered in the various stages of viscose preparation; they may tend to lose their dispersing power in viscose on standing during the normal viscose storage and ripening periods; their dispersing powers may be too low, thus requiring the incorporation of excessive amounts which may adversely affect the spinning process or the character of the yarn or both; they may be ineffective as inhibitors of incrustations on spinnerets and other devices operatively associated with the coagulating bath or they may in fact be incompatible with and reduce the efficiency of the incrustation inhibiting agent employed in a coagulating bath.

In accordance with the present invention it has been found that the above mentioned difficulties may be obviated and that an improved viscose spinning solution may be produced by incorporat-

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ing into the viscose at any stage of its preparation a product formed from the reaction of at least about 12 moles of an alkylene oxide with one mole of a primary or secondary aliphatic amine or mixtures thereof, the amines being alkyl or alkenyl amines containing from 6 to 18 carbon atoms.

Among the alkylene oxides which are particularly suitable in forming the amine-alkylene oxide reaction products employed in the present invention are ethylene and propylene oxide. Advantageous results are derived where the amine-alkylene oxide compounds employed represent the reaction of between about 12 and 100 moles of an alkylene oxide per mole amine and with particular advantage where the moles of alkylene oxide per mole of amine are between about 14 and 75 and preferably between about 18 and 60.

The above defined primary or secondary amines or mixtures thereof which are reacted with an alkylene oxide may if desired contain other substituents in addition to the alkyl and alkenyl radicals specified such as, for example, aryl radicals or other amine radicals. In the latter situation there may be mentioned the mono-, di-, tri-, etc. amines. Examples of various typical amines which may be reacted to produce the amine derivatives employed in the present invention will appear later in the specification.

In general the amine reactants having alkyl or alkenyl radicals containing more than 6 carbon atoms are preferred such as for example radicals containing from 12 to 18 carbon atoms, or more advantageously from 14 or 16 up to 18 carbon atoms. Advantageous results may also be derived by the employment of amine-alkylene oxide compounds made from mixtures of amines having a mean molecular weight of at least about 175 or 185 and more advantageously of at least about 200. With similar advantage mixtures of amines may be used as starting materials in which at least about 80 mole percent of the amines have radicals containing from 12 to 18 carbon atoms and in addition thereto either 20 mole percent containing from 14 to 18 carbon atoms or the amine mixture having a mean molecular weight of about 175. Particularly advantageous results are derived where 80 mole percent of the amine mixtures have radicals containing 14 to 18 carbon atoms or in addition 20 mole percent containing from 16 to 18 carbon atoms.

Similar advantages are derived where the amine mixture has a mean molecular weight of at least 185 and 90 mole percent thereof have

radicals containing from 14 to 18 carbon atoms or where the mixture has a mean molecular weight of at least 200 with about 70 mole percent having radicals from 16 to 18 carbon atoms. Especial advantages are derived where 90 mole percent of the mixture have radicals of 18 carbon atoms.

In practicing the present invention the amine-alkylene oxide reaction product may be added if desired at one or more of the viscose preparation stages such as, for example, (a) to a chemically prepared wood pulp which has been refined for the manufacture of viscose, (b) prior to or during the shredding of the alkali cellulose, (c) to cellulose xanthate crumbs before or during the dissolving step, and (d) to dissolved cellulose xanthate (viscose) before or after filtration or both. Particularly advantageous results are derived where the reaction product is added to and admixed with a viscose solution prior to filtration.

The compounds useful in practicing the invention may, in general, be prepared in the following manner. A weighed quantity of one or more of the amines mentioned is mixed with a small amount of an alkaline catalyst such as, for example, about 0.5 to 2%, by weight, sodium hydroxide in the form of a solid or of a 50% aqueous solution. Other alkali or alkaline earth metal catalysts may be used in the place of sodium hydroxide, such as for example, potassium hydroxide or the alkali metal alcoholates, e. g. sodium methylate. The mixture is introduced into a pressure resistant vessel such as an autoclave which is equipped with suitable agitating, heating and cooling means. The contents of the autoclave are then heated while stirring to an initial reaction temperature of from about 100° C. to about 200° C., the range between about 125° C. to about 150° C. being preferred to facilitate the control of the reaction. After the initial reaction temperature is attained a weighed amount of an alkylene oxide such as, for example, ethylene or propylene oxide is then introduced into the autoclave preferably through a suitable meter while the mixture is agitated. The rate of addition of the alkylene oxide depends among other things upon the efficiency of the means for dissipating the heat of the reaction. The duration of the reaction may extend over a period of from 1 to 3 hours or more depending among other things upon the amount and character of each of the reactants. The temperature during the reaction is preferably maintained at about 125° C. and the pressure is not permitted to exceed about 200 pounds per square inch. After all of the alkylene oxide has been introduced the temperature control and agitation of the contents of the autoclave is continued until the reaction is complete as is indicated by a gradual drop in pressure and by a rapid decrease in temperature. The contents of the autoclave may then be discharged and permitted to cool to room temperature. The reaction products are all soluble in water or alcohol and also in various aqueous acid or alkaline liquids.

Depending upon the character and molecular weight of the amine or mixture of amines and upon the number of moles of alkylene oxide which are reacted the character of the reaction product may range from a viscous liquid to a semisolid or solid. In practicing the present invention a quantity of the amine-alkylene oxide reaction product which is dissolved in a suitable solvent such as for example water is added to and mixed with viscose forming materials at one or more of

the stages of the viscose preparation so as to form a viscose spinning solution containing for example between about 0.01 and 0.2%, by weight, of the reaction product based on the weight of the viscose.

The following specific examples in which parts by weight are given will serve to illustrate the present invention, although it will be understood that the invention is not limited to the specific conditions set forth.

Example 1

534 parts of normal primary octadecenylamine is mixed with 5 parts of a 50% aqueous sodium hydroxide solution as a catalyst and placed in an autoclave where it is heated to an initial reaction temperature of 120° C. while stirring the mixture. Then 1056 parts of ethylene oxide is gradually introduced into the autoclave over a period of one hour and forty minutes and the temperature is permitted to rise to about 144° C. while the maximum pressure attained is about 100 pounds per square inch. After all of the ethylene oxide has been introduced and the reaction is completed as is indicated by a gradual decrease in pressure to zero gauge, the material is evacuated from the autoclave and permitted to cool to room temperature. The reaction product thus formed is a brownish waxy solid which is soluble in water and represents the reaction of about 12 moles of ethylene oxide per mole of amine.

A suitable quantity of the reaction product is dissolved in water to make up a 30%, by weight, stock solution and the stock solution gradually added to and mixed with a filtered viscose spinning solution until the viscose contains about 0.05%, by weight, of the reaction product based on the weight of the viscose, the viscose containing about 8% cellulose and about 6.5% sodium hydroxide. The viscose spinning solution prepared in this manner is clear and transparent, and when extruded into a coagulating bath containing, by weight, about 10% sulfuric acid, 20% sodium sulfate and 1% zinc sulfate, does not clog the spinneret orifices after prolonged continuous periods of spinning. In addition the presence of the amine reaction product in the viscose and in the coagulating bath inhibits the formation of incrustations on the spinneret face and on other devices operatively associated with the coagulating bath liquid. The yarn produced is desirably uniform in appearance and strength.

Example 2

The procedure of Example 1 is followed with the exception that 2112 parts of ethylene oxide is introduced into the autoclave over a period of about 2½ hours. The reaction product representing the reaction of about 24 moles of ethylene oxide per mole of amine is similar to the product of Example 1 both in character and in its effectiveness with the exception that only about 0.025%, by weight, of the product is incorporated in the viscose.

Example 3

The procedure of Example 1 is followed with the exception that 267 parts of the octadecenylamine is reacted with 1180 parts of propylene oxide, the latter being introduced over a period of 3½ to 4 hours. The initial reaction temperature is about 160° C. and the temperature is not permitted to rise above about 180° C. while the pressure is not permitted to rise above about 85 pounds per square inch. The reaction product is similar in character and effectiveness to that of

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Example 1 and represents the reaction of about 20 moles of propylene oxide per mole of the amine.

Example 4

5 parts of a 50% sodium hydroxide solution is mixed with 71 parts of secondary dodecyl amine and 215 parts of normal primary octadecyl amine and the mixture placed in an autoclave where it is heated to an initial reaction temperature of 130° C. while stirring the mixture. Then 1320 parts of ethylene oxide is gradually introduced into the autoclave over a period of about 2 hours and the temperature is permitted to rise to about 150 C. while the maximum pressure attained is about 150 pounds per square inch. After all of the ethylene oxide has been introduced and the reaction is completed as is indicated by a gradual decrease in pressure to zero gauge, the material is evacuated from the autoclave and permitted to cool to room temperature. The reaction product formed is a brown waxy solid which is soluble in water and represents the reaction of about 30 moles of ethylene oxide per mean mole of the mixture of amines having a mean molecular weight of about 286. An aqueous solution of the resulting reaction product is prepared and incorporated in a viscose solution in the manner and under the conditions of Example 1 with the exception that concentration of the product in the viscose is about 0.06%, by weight.

Example 5

5 parts of a 50% aqueous sodium hydroxide solution as a catalyst is mixed with the following normal primary amines; 133 parts of octadecadienyl amine; 48 parts of hexadecyl amine, 21 parts of tetradecyl amine, and 37 parts of dodecyl amine. The mixture is then placed in an autoclave where it is heated to an initial reaction temperature of about 130° C. while stirring the mixture. Then 1760 parts of ethylene oxide is gradually introduced into the autoclave over a period of about 2½ hours and the temperature is permitted to rise to about 160 C. while the maximum pressure attained is about 150 pounds per square inch. After all of the ethylene oxide has been introduced and the reaction is completed as indicated by a gradual decrease in pressure to zero gauge, the material is evacuated from the autoclave and permitted to cool to room temperature. The reaction product formed is a waxy solid which is soluble in water and represents the reaction of about 40 moles of ethylene oxide per mean mole of the mixture of amines having a mean molecular weight of about 240. The resulting reaction product is dissolved in water to form an aqueous solution containing about 30%, by weight, of the product and this solution is gradually added to and mixed with a freshly prepared viscose solution prior to the filtration thereof. The composition of the viscose is the same as that described in Example 1. A sufficient quantity of the reaction product is added to form a viscose solution containing about 0.05%, by weight, of the product based on the weight of the viscose. The viscose solution prepared in this manner results in longer periods of continuous viscose filtration and also in a filtered viscose spinning solution which is clear, transparent. The yarn produced is desirably uniform and has improved strength.

Example 6

5 parts of a 50% aqueous sodium hydroxide solution as a catalyst is mixed with the follow-

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ing normal primary amines; 5 parts of hexyl amine, 6 parts of octylamine, 16 parts decylamine, 83 parts of dodecylamine, 43 parts of tetradecylamine and 40 parts of octadecylamine. The mixture is then reacted with 2200 parts of ethylene oxide in the manner and under the conditions described in Example 5. The reaction product represents the reaction of about 50 moles of ethylene oxide with one mean mole of the mixture of amines having a mean molecular weight of about 194.

A quantity of the reaction product is dissolved in water to form a 30%, by weight, aqueous stock solution and the stock solution is gradually added to and mixed with a viscose solution of the composition described in Example 1. The addition is made both before filtration and after filtration of the viscose in quantities sufficient to form a filtered viscose spinning solution containing about 0.04%, by weight, of the reaction product.

Example 7

The procedure of Example 5 is followed with the exception that 2640 parts of ethylene oxide is introduced into the autoclave over a period of about 3½ hours and reacted with the following normal primary amines; 8 parts of decylamine, 28 parts of dodecylamine, 85 parts of tetradecylamine, 72 parts of hexadecylamine and 27 parts of octadecylamine. The product represents the reaction of about 60 moles of ethylene oxide with one mean mole of the mixture of amines having a mean molecular weight of about 220.

Example 8

The procedure in this example is the same as that set forth in Example 7 with the exception that 3520 parts of ethylene oxide is introduced into the autoclave over a period of about 4½ hours to produce a reaction product having about 80 moles of ethylene oxide per mean mole of the mixture of amines.

Example 9

The procedure of Example 5 is followed with the exception that the following mixture of primary normal amines are reacted; 24 parts of hexadecylamine, 27 parts of octadecylamine, 80 parts of octadecylamine, and 133 parts of octadecadienyl amine. The resulting reaction product which is incorporated in the viscose represents the reaction of about 40 moles of ethylene oxide per mean mole, the amine mixture having a mean molecular weight of about 264.

Example 10

A suitable quantity of the amine-ethylene oxide reaction product of Example 9 was dissolved in water to form a 50%, by weight, aqueous solution and the aqueous solution sprayed onto a batch of alkali cellulose (soda cellulose) prior to the shredding operation. The quantity of the reaction product employed is sufficient to form a shredded alkali cellulose containing about 0.8%, by weight, of the reaction product based on the weight of the cellulose. By preparing viscose in this manner a finer and more uniformly shredded alkali cellulose is obtained which in turn permits a more uniform and more complete xanthation of the alkali cellulose and dissolution of the cellulose xanthate into viscose. In addition more rapid and more prolonged periods of continuous viscose filtration are achieved and a clear and transparent viscose results which may be spun into yarn of desirable uniformity and strength.

Example 11

The procedure of Example 10 is followed with the exception that the aqueous solution of the amine-ethylene oxide reaction product is gradually introduced into a cellulose xanthate dissolving vessel and mixed with the cellulose xanthate crumbs and the aqueous caustic soda solvent therefor, prior to the completion of the dissolving step. A sufficient quantity of the reaction product is employed to form a viscose containing about 0.08%, by weight, of the reaction product. The results obtained are similar to those of Example 10 as regards the filtration of the viscose, the uniformity and clarity of the filtered viscose, and character of the yarn product.

Example 12

A suitable quantity of the amine-ethylene oxide reaction product of Example 9 was dissolved in water to form a 50%, by weight, aqueous solution and the aqueous solution sprayed onto a quantity of chemically refined wood pulp containing about 98% alpha cellulose and is permitted to dry thereon. The quantity of the reaction product added is sufficient to form a treated wood pulp containing about 0.2%, by weight, of the reaction product based on the weight of the bone dry cellulose. To an unfiltered viscose solution prepared from the above treated wood pulp is then added a sufficient quantity of the 50% aqueous solution of the amine derivative to form a viscose containing about 0.05%, by weight, of the amine derivative based on the weight of the viscose. The results obtained are similar to those described in Example 10.

In practicing the present invention the amine-alkylene oxide reaction product may, if desired, be employed in the preparation of various types of viscose solutions; such as for example those containing and those not containing delustering materials such as for example finely divided and dispersed particles of titanium dioxide, waxes, oils, etc. Under certain conditions the incorporation of the amine-alkylene oxide reaction product may with advantage improve the degree, stability, and uniformity of the dispersion of the delustering particles in the viscose.

As previously stated the amine derivatives may be added to and incorporated in chemically prepared cellulose such as wood pulp, cotton, etc. prior to the formation of alkali cellulose therefrom, or, if desired, they may be added to the alkali cellulose. In either situation it is found advantageous to incorporate between about 0.01 and 1.0%, by weight, of the amine derivatives, based on the weight of the bone dry cellulose and with particular advantage between about 0.05 and 0.8%.

Further advantages are however derived where relatively small amounts of the amine derivatives are added both at some point before the xanthation step and also after the dissolution of the cellulose xanthate into viscose. Advantageously the amounts added at the several stages of viscose preparation may be such as to form a viscose solution containing between about 0.01 and 0.2%, by weight, of the amine derivative based on the weight of the viscose solution.

Other amines which may be reacted with an alkylene oxide to produce the products useful in the present invention may include normal monoamines of the aliphatic series such as hexylamine, heptylamine, octylamine, nonylamine,

decylamine, undecylamine, dodecylamine, tridecylamine, tetradecylamine, pentadecylamine, hexadecylamine, heptadecylamine, octadecylamine; or, diamines of the aliphatic series including 1,6 hexanediamine, 1,7 heptane diamine, 1,8 octyl diamine, 1,9 nonyl diamine, 1,10 dodecylamine, 1,11 undecyl diamine, 1,12 dodecyl diamine, 1,13 tridecyl diamine, 1,14 tetradecyl diamine, 1,15 pentadecyl diamine, 1,16 hexadecyl diamine, 1,17 heptadecyl diamine, 1,18 octadecyl diamine, or normal monoamines derived from the olefinic series such as hexenyl amine, heptenyl amine, octenyl amine, nonenyl amine, decenyl amine, undecenyl amine, dodecenyl amine, tridecenyl amine, pentadecenyl amine, hexadecenyl amine, heptadecenyl amine, and octadecenyl amine, or diamines derived from the olefinic series such as 1,6 amino hexene, 1,7 amino heptene, 1,8 amino octene, 1,9 amino nonene, 1,10 amino decene, 1,11 amino undecene, 1,12 amino dodecene, 1,13 amino tridecene, 1,14 amino tetradecene, 1,15 amino pentadecene, 1,16 amino hexadecene, 1,17 amino heptadecene, and 1,18 amino octadecene.

We claim:

1. A viscose spinning solution having incorporated therein between about 0.01 and 0.2%, by weight, of a product formed by the reaction of at least about 12 moles of an alkylene oxide with one mean mole of a mixture of primary aliphatic amines selected from the group consisting of alkyl and alkenyl amines containing from 6 to 18 carbon atoms; at least about 80 mole percent of said mixture of amines containing from 12 to 18 carbon atoms.

2. A viscose spinning solution having incorporated therein between about 0.01 and 0.2%, by weight, of a product formed from the reaction of between about 12 and 100 moles of an alkylene oxide with one mean mole of a mixture of primary aliphatic amines selected from the group consisting of alkyl and alkenyl amines containing from 6 to 18 carbon atoms, at least about 80 mole percent of said mixture of amines containing from 6 to 18 carbon atoms, at least about 80 mole percent of said mixture of amines containing from 14 to 18 carbon atoms.

3. A viscose spinning solution having incorporated therein between about 0.01 and 0.2%, by weight, of a product formed from the reaction of between about 12 and 100 moles of an alkylene oxide with one mean mole of a mixture of primary aliphatic amines selected from the group consisting of alkyl and alkenyl amines containing from 6 to 18 carbon atoms; at least about 80 mole percent of said mixture of amines containing from 14 to 18 carbon atoms and at least about 20 mole percent containing from 16 to 18 carbon atoms.

4. A viscose spinning solution having incorporated therein between about 0.01 and 0.2%, by weight, of a product formed from the reaction of between about 14 and 75 moles of an ethylene oxide with one mean mole of a mixture of primary aliphatic amines selected from the group consisting of alkyl and alkenyl amines containing from 6 to 18 carbon atoms, said mixture of amines having a mean molecular weight of at least about 200 and at least about 70 mole percent of said mixture of amines containing from 16 to 18 carbon atoms.

5. A viscose spinning solution according to claim 11 in which ethylene oxide is used as the alkylene oxide reactant.

6. A viscose spinning solution according to

claim 1 in which ethylene oxide is used as the alkylene oxide reactant.

7. A viscose spinning solution according to claim 1 in which propylene oxide is used as the alkylene oxide reactant.

8. A viscose spinning solution having incorporated therein between about 0.01 and 0.2%, by weight, of a product formed from the reaction of between about 12 and 100 moles of ethylene oxide with one mole of normal primary octadecylamine. 10

9. A viscose spinning solution having incorporated therein between about 0.01 and 0.2%, by weight, of a product formed from the reaction of between about 12 and 100 moles of ethylene oxide with one mole of normal primary octadecylamine. 15

10. A viscose spinning solution having incorporated therein between about 0.01 and 0.2%, by weight, of a product formed from the reaction of between about 12 and 100 moles of ethylene oxide with one mole of normal primary octadecadienylamine. 20

11. A viscous spinning solution having incorporated therein a relatively small amount of a product formed by the reaction of at least about 12 moles of an alkylene oxide with one mole of an aliphatic amine selected from the group consisting of alkyl and alkenyl amines containing from 6 to 18 carbon atoms. 25

12. A viscose spinning solution having incorporated therein between about 0.01 and 0.2%, by weight, of a composition comprising a product formed by the reaction of between about 12 and 100 moles of an alkylene oxide with one mole of a

primary aliphatic amine selected from the group consisting of alkyl and alkenyl amines containing from 12 to 18 carbons atoms.

13. A viscose spinning solution having incorporated therein between about 0.01 and 0.2%, by weight, of a product formed from the reaction of between about 12 and 100 moles of an alkylene oxide with one mean mole of a mixture of primary aliphatic amines selected from the group consisting of alkyl and alkenyl amines containing from 6 to 18 carbon atoms; said mixture of amines having a mean molecular weight of at least about 185.

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