Patented Feb. 9, 1943 2,310,207

UNITED STATES PATENT OFFICE

2,310,207

SURFACE-ACTIVE INCRUSTATION INHIBITOR

Rudolph S. Bley, Milligan College, Tenn., assignor to North American Rayon Corporation, New York, N. Y., a corporation of Delaware

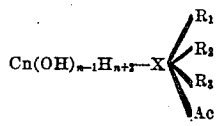
No Drawing. Original application October 7, 1938, Serial No. 233,826. Divided and this application January 29, 1940, Serial No. 316,279

10 Claims. (Cl. 18—54)

This is a division of my application Ser. No. 233,826 filed October 7, 1938.

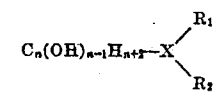
In the manufacture of cellulosic products, such as filaments, threads and the like, a viscose solution is continuously extruded through the minute orifices of a spinneret into a coagulating or setting bath. However, since the introduction of the viscose process great troubles have been and are still experienced as far as continuous spinning is concerned due to impurities, such as, for example, precipitated cellulose particles, sulphur and resin particles, zinc compounds, etc., present in either the viscose solution or the spin bath. These impurities gradually contaminate the spinnerets, clog and reduce the widths of the spinneret orifices with the result that filaments of uneven thickness are obtained. If contamination proceeds the individual filaments start to tear and occasion interruption of the spinning process.

I have found that contamination of spinnerets and clogging of spinneret orifices may be substantially overcome by spinning viscose solutions in the presence of cation-active monosaccharide derivatives or acid addition products thereof having the general structure:



in which n is 5 or 6, R_1 is a higher aliphatic radical having 8 or more carbon atoms, R_2 and R_3 represent lower aliphatic and/or aromatic radicals or hydrogen atoms, X represents an atom of nitrogen, phosphorus, arsenic or antimony, and Ac represents an innocuous anion, such as an OH group or a negative acid radical.

Although these compounds may be obtained in a variety of ways, they are most readily obtained by reacting an aliphatic or aromatic halide having less than 8 carbon atoms with an amine, phosphine, arsine or stibine having the structure:



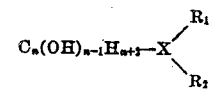
in which n, X, R_1 and R_2 have the foregoing significance.

Cation-active compounds are surface-active compounds which carry in the cation a hydrocarbon chain 8 or more carbon atoms. They are particularly advantageous because they may be used in neutral salt, alkaline and acidic aqueous solutions, and also in hard water. In contradistinction to cation-active compounds, anion-active compounds are surface-active compounds which carry in the anion a more or less extended hydrocarbon chain. They flocculate in neutral salt, alkaline and acidic aqueous solutions, and also in hard water. Common soaps, etc., are anion-active compounds, and thus are unable to prevent the incrustation of spinnerets and spinneret orifices.

Incrustation inhibitors, in accordance with the present invention, may be prepared from amines, phosphines, arsines and stibines derived from monosaccharides of the ketose or aldose type containing 5 or 6 carbon atoms. These sugar amines, phosphines, arsines and stibines may be prepared from glucose, galactose, fructose, xylose, arabinose, mannose, rhamnose, ribose, talose, etc. Acid addition compounds may be prepared from these sugar amines, phosphines, arsines and stibines by treating them with inorganic or organic acids, such as hydrochloric acid, sulphuric acid, acetic acid, formic acid, etc. For conversion into cation-active compounds these sugar amines, phosphines, arsines and stibines are reacted with an alkyl halide containing 8 or more carbon atoms. Acid addition compounds may be formed from these secondary, cation-active amines, phosphines, arsines and stibines. These cation-active secondary bases may also be reacted with lower aliphatic or aromatic halides or sulphates for the production of cation-active, tertiary bases from which acid addition products may be formed. The cation-active, tertiary bases may finally be reacted with an aliphatic or aromatic—preferably low-molecular—halide or sulphate to form cation-active, quaternary ammonium, phosphonium, arsonium or stibonium salts which may be converted into corresponding cation-active, quaternary bases. The following table depicts a number of compounds which may be used as incrustation inhibitors:

TABLE

1. Cation-active, secondary bases having the structure:

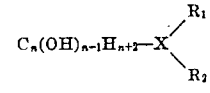


in which n is 5 or 6, R_1 is a higher aliphatic radical having 8 or more carbon atoms, R_2 represents hydrogen and X represents an atom of nitrogen,

phosphorus, arsenic or antimony, and acid addition products thereof.

N-octyl glucyl amine
N-nonyl glucyl amine
N-decyl glucyl amine
N-tetradecyl glucyl amine
N-cetyl glucyl amine
N-dodecyl glucyl amine
N-octadecyl glucyl amine
N-eicosyl glucyl amine
N-ceryl glucyl amine
N-octadecenyl glucyl amine
Octyl glucyl phosphine
Octyl glucyl arsine
Octyl glucyl stibine
Octyl glucyl sulphide
Nonyl glucyl phosphine
Nonyl glucyl arsine
Nonyl glucyl stibine
Decyl glucyl phosphine
Decyl glucyl arsine
Decyl glucyl stibine
Decyl glucyl sulphide
Cetyl glucyl phosphine
Cetyl glucyl arsine
Cetyl glucyl stibine
Dodecyl glucyl phosphine
Dodecyl glucyl stibine
Dodecyl glucyl arsine
N-octyl fructyl amine, etc.

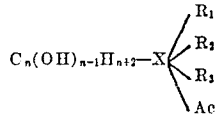
2. Cation-active, tertiary bases having the structure:



in which n is 5 or 6, R_1 is a higher aliphatic radical having 8 or more carbon atoms, R_2 represents a lower aliphatic or aromatic radical and X represents an atom of nitrogen, phosphorus, arsenic or antimony, and acid addition products thereof.

N-octyl N-hydroxy-ethyl glucyl amine
N-decyl N-hydroxy-ethyl glucyl amine
N-octyl methyl glucyl amine
N-decyl-ethyl glucyl amine
N-tetradecyl N-hydroxy-ethyl glucyl amine
N-cetyl N-hydroxy-ethyl glucyl amine
N-octadecyl N-hydroxy-ethyl glucyl amine
N-dodecyl N-hydroxy-ethyl glucyl amine
N-eicosyl N-hydroxy-ethyl glucyl amine
N-ceryl N-hydroxy-ethyl glucyl amine
N-octyl N-hydroxy-ethyl fructyl amine
N-octyl phenyl glucyl amine
N-octyl hydroxy-phenyl glucyl amine
Corresponding phosphines, arsines, stibines and sulphides, etc.

3. Cation-active, quaternary "onium" bases and salts having the structure:



in which n is 5 or 6, R_1 is a higher aliphatic radical having 8 or more carbon atoms, R_2 and R_3 represent lower aliphatic and/or aromatic radicals, X represents an atom of nitrogen, phosphorus, arsenic or antimony and Ac represents an innocuous anion, such as an OH group or a negative acid radical.

N-methyl-N-ethyl-N-glucyl cetyl ammonium chloride
N-methyl-N-ethyl-N-glucyl octyl ammonium bromide
N-methyl-N-ethyl-N-glucyl dodecyl ammonium bromide
N-methyl-N-ethyl-N-glucyl stearyl ammonium iodide
N-methyl-N-hydroxyethyl-N-glucyl cetyl ammonium bromide
N-methyl-N-ethyl-N-glucyl cetyl ammonium sulphate
N:N-dimethyl-N-glucyl stearyl ammonium iodide
N:N-diethyl-N-glucyl oleyl ammonium chloride
N-methyl-N-butyl-N-xylyl cetyl ammonium bromide
N-methyl-N-ethyl-N-galactyl oleyl ammonium iodide
N-methyl-N-(1-propane 2:3 diol)-N-glucyl cetyl ammonium iodide
N-methyl-phenyl-N-glucyl octyl ammonium bromide
N-methyl-tolyl-N-fructyl decyl ammonium chloride
Methyl-ethyl-glucyl cetyl phosphonium bromide
Ethyl-propyl-fructyl dodecyl phosphonium chloride
Ethyl-butyl-glucyl octyl arsonium bromide
Methyl-ethyl-glucyl arsonium sulphate
Methyl-ethyl-glucyl octyl stibonium bromide
Methyl-ethyl-glucyl dodecyl stibonium iodide
Methyl-ethyl-glucyl cetyl sulphonium bromide
Methyl-ethyl-fructyl octyl sulphonium chloride
N-methyl-N-ethyl-N-glucyl cetyl ammonium hydroxide
Methyl-ethyl-fructyl dodecyl phosphonium hydroxide, etc.

Although these cation-active incrustation inhibitors may form corresponding bases in viscose solutions and salts in acid spin baths, they retain their surface activity and, thus, their property of substantially preventing incrustations on prolonged spinning. If very small amounts of these cation-active compounds are added to viscose solutions or spin baths the physical characteristics such as strength, plasticity, lustre, etc., of regenerated cellulose produced therefrom or therein, respectively, remains unaltered.

Upon increasing the amount of incrustation inhibitor in a given viscose solution or spin bath, the regenerated cellulose produced therefrom or therein, respectively, may alter its physical characteristics, i. e., it may acquire a soft-lustre, become more plastic, lose part of its original strength, etc. For such reasons, the amounts to be added to viscose solutions or spin baths must be predetermined by experimentation. Additions of about 0.3 to 5.0 grams per liter of viscose solution are generally sufficient to allow continuous spinning without substantially affecting the inherent physical characteristics of regenerated cellulose threads or films. Although these cation-active incrustation inhibitors improve the spinning of any conventional viscose solution or spin bath, I have found that they are especially valuable as additions to zinc-bearing spin baths, i. e., spin baths containing a soluble zinc compound, for example, zinc sulphate, these baths having poor spinning qualities. I am well aware, that cation-active glucyl amines, etc., have been heretofore prepared (vide U. S. Patents Nos. 2,016,956; 2,060,850; 2,060,851) as wetting agents. However, this prior art does not disclose the prevention of incrustations by means of cation-active compounds.

Example I

A mixture of 180 parts of ethylene chlorhydrin, 125 parts of potassium hydroxide, 700 parts of N-dodecyl-glucyl-amine, and 5000 parts of methyl alcohol is refluxed at a moderate temperature for a few hours. The solution is filtered to remove inorganic salts and the filtrate evaporated to dryness. About 0.3 to 2.0 grams of the waxy N-dodecyl-N-hydroxy-ethyl glucyl amine are added to about one liter of a viscose solution of conventional concentration and maturity. This solution is then extruded through a spinneret into a conventional spin bath, such as, for example, a glucose bath, a magnesium-bath, etc. The spinnerets and their orifices remain clean on prolonged spinning. Other cation-active compounds having the structure set forth above, may be used with equal success.

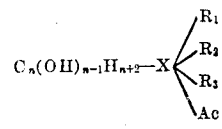
Example II

A mixture of about 200 parts of glycerol-monochlorhydrin, 100 parts of potassium hydroxide, 720 parts of N-octadecyl-glucyl-amine and 5000 parts of methyl alcohol is refluxed to form octadecyl-glucyl-amine, propanediol. A conventional viscose solution is extruded through fine orifices of precious metal spinnerets into an acid spin bath, containing for example, sulphuric acid, sodium sulphate, ammonium sulphate and zinc sulphate and about 0.3 to 5.0 grams per liter of waxy N-octadecyl-glucyl-amine, propanediol. Spinning irregularities and difficulties are substantially overcome. Without the addition of an incrustation inhibitor spinning is interrupted after a very short period of time. N-octadecyl-glucyl-amino, propanediol may be replaced by any other sufficiently soluble and stable ammonium, phosphorus, sulphur, arsenic and antimony derivative of a monosaccharide having the general structure set forth above.

Example III

A solution of about 150 parts of N-methyl-N-glucyl cetyl amine in about 500 parts of ethyl alcohol is boiled under reflux with about 150 parts of ethyl iodide for several hours. After revolving excess ethyl iodide and alcohol by evaporation, N-methyl-ethyl-N-glucyl cetyl ammonium iodide is obtained as a brownish mass. This compound or any other one set forth above is added to both the viscose solution and the spin bath. The formation of zinc rings and sulphur craters is substantially overcome.

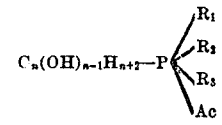
Although these examples will serve to illustrate the present invention, I do not wish to be limited to the incrustation inhibitors and concentrations thereof recited therein, since I may make use of any cation-active compound having the structure



in which n, X, R_1, R_2, R_3 and Ac have the aforementioned significance provided it is sufficiently soluble and stable in spin baths and/or viscose solutions to furnish surface-active cations therein. Modifications of my invention will readily be recognized by those skilled in the art, and I desire to include all such modifications and variations coming within the scope of the appended claims.

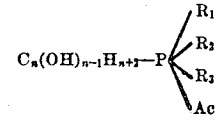
I claim:

1. An acid viscose spin bath, for coagulating viscose filaments therein, containing a dissolved, substantially stable, cation-active mono-saccharide derivative having the structure:



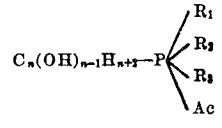
in which n is a number selected from the group consisting of 5 and 6, R_1 is a higher aliphatic radical having at least 8 carbon atoms, R_2 and R_3 represent substituents selected from the group consisting of lower aliphatic radicals, lower aromatic radicals and hydrogen, and Ac represents a substituent selected from the group consisting of OH and negative acid radicals, whereby incrustation of the spinneret during the spinning operation is substantially inhibited.

2. An acid viscose spin bath, for coagulating viscose filaments therein, containing a dissolved, substantially stable, cation-active monosaccharide derivative having the structure:



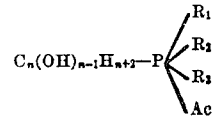
in which n is a number selected from the group consisting of 5 and 6, R_1 is a higher aliphatic radical having at least 8 carbon atoms, R_2 and R_3 represent lower aliphatic radicals, and Ac represents a substituent selected from the group consisting of OH and negative acid radicals, whereby incrustation of the spinneret during the spinning operation is substantially inhibited.

3. An acid viscose spin bath, for coagulating viscose filaments therein, containing a dissolved, substantially stable, cation-active monosaccharide derivative having the structure:



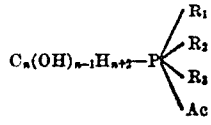
in which n is a number selected from the group consisting of 5 and 6, R_1 is a higher aliphatic radical having at least 8 carbon atoms, R_2 and R_3 represent lower aromatic radicals, and Ac represents a substituent selected from the group consisting of OH and negative acid radicals, whereby incrustation of the spinneret during the spinning operation is substantially inhibited.

4. An acid viscose spin bath, for coagulating viscose filaments therein, containing a dissolved, substantially stable, cation-active monosaccharide derivative having the structure:



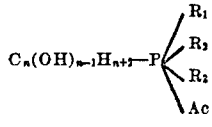
in which n is a number selected from the group consisting of 5 and 6, R_1 is a higher aliphatic radical having at least 8 carbon atoms, R_2 and R_3 represent hydrogen, and Ac represents a substituent selected from the group consisting of OH and negative acid radicals, whereby incrustation of the spinneret during the spinning operation is substantially inhibited.

5. An acid viscose spin bath containing a water-soluble zinc compound and a dissolved, substantially stable cation-active monosaccharide derivative having the structure:



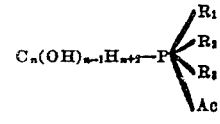
in which n is a number selected from the group consisting of 5 and 6, R_1 is a higher aliphatic radical having at least 8 carbon atoms, R_2 and R_3 represent substituents selected from the group consisting of lower aliphatic radicals, lower aromatic radicals and hydrogen, and Ac represents a substituent selected from the group consisting of OH and negative acid radicals.

6. An acid viscose spin bath containing a water-soluble zinc compound and a dissolved, substantially stable cation-active monosaccharide derivative having the structure:



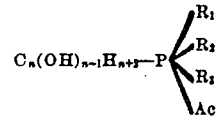
in which n is a number selected from the group consisting of 5 and 6, R_1 is a higher aliphatic radical having at least 8 carbon atoms, R_2 and R_3 represent lower aromatic radicals, and Ac represents a substituent selected from the group consisting of OH and negative acid radicals.

7. An acid viscose spin bath containing a water-soluble zinc compound and a dissolved, substantially stable cation-active monosaccharide derivative having the structure:



in which n is a number selected from the group consisting of 5 and 6, R_1 is a higher aliphatic radical having at least 8 carbon atoms, R_2 and R_3 represent lower aromatic radicals, and Ac represents a substituent selected from the group consisting of OH and negative acid radicals.

8. An acid viscose spin bath containing a water-soluble zinc compound and a dissolved, substantially stable cation-active monosaccharide derivative having the structure:



in which n is a number selected from the group consisting of 5 and 6, R_1 is a higher aliphatic radical having at least 8 carbon atoms, R_2 and R_3 represent hydrogen, and Ac represents a substituent selected from the group consisting of OH and negative acid radicals.

9. An acid viscose spin bath containing dissolved methyl-ethyl-fructyl dodecyl phosphonium chloride.

10. An acid viscose spin bath containing sulphuric acid, zinc sulphate and methyl-ethyl-fructyl dodecyl chloride.

RUDOLPH S. BLEY.