Patented Dec. 30, 1952

2,623,874

UNITED STATES PATENT OFFICE

2,623,874

CELLULOSE-MORPHOLINIUM DERIVATIVE COMPOSITION AND PROCESS

Kenneth R. Brown, West Chester, Pa., assignor to Atlas Powder Company, Wilmington, Del., a corporation of Delaware

No Drawing. Application January 16, 1950, Serial No. 138,940

15 Claims. (Cl. 260—212)

1

The present invention relates to improvements in the processing of refined chemical pulp and more particularly to the manufacture of cellulose pulp for use in the manufacture of regenerated cellulose filament and/or films by the viscose process.

Cellulose to be converted into rayon or cellophane film by the viscose process is usually supplied to the manufacturer of such materials in the form of refined cellulose fibers matted together into thick sheets. Much of the cellulose so provided is prepared by sulfite digestion of wood pulp whereby the non-cellulosic portion of the wood is dissolved away leaving the cellulose fibers which may be further purified and bleached before felting into the sheet form usually delivered to manufacturers of regenerated cellulosic products under the designation refined chemical pulp.

It is the object of the present invention to provide a specially treated refined cellulose pulp.

It is a more particular object of the invention to provide a refined chemical cellulose pulp which has been treated with and retains a minor proportion of certain soluble and stable morpholinium or thiomorpholinium derivatives.

It is a further object to provide an improved viscose process for producing regenerated cellulose based on the use of such treated cellulose pulp.

The above and other objects will become more apparent in the course of the following specification and the appended claims.

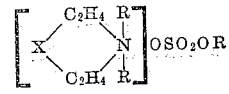
In the viscose process for preparing filaments and films of regenerated cellulose, refined chemical pulp is first converted to alkali cellulose by immersing the sheets of pulp in strong alkali solution until they are thoroughly saturated after which the excess of alkali is removed by subjecting the impregnated sheets to hydraulic pressure. The alkali cellulose is then shredded to a fluffy fibrous condition and allowed to "age" during which period the product undergoes important oxidative processes. The aged alkali cellulose is then converted to sodium cellulose xanthate by reaction with carbon disulfide and the xanthate dissolved in dilute aqueous sodium hydroxide to form viscose solution. The viscose solution is allowed to age or ripen for several hours or even days under carefully controlled temperature conditions during which time it is repeatedly filtered to remove any undissolved fibers, dust or other foreign matter and clumps of gelled, partially xanthated fibers. Finally the viscose is regenerated into filaments or sheets by extruding

2

through orifices of proper dimension into coagulating baths of acid or acid-salt mixture.

In my copending application Serial No. 56,668, filed October 26, 1948, now Patent No. 2,495,833 issued January 31, 1950 I have disclosed that certain surface active morpholinium or thiomorpholinium derivatives may be advantageously incorporated in the coagulating bath or in the viscose solution being extruded into the coagulating bath; whereby encrustation of the orifice is avoided, with consequent improvement in quality of product and facility of operation.

In accordance with the present invention I find it advantageous to incorporate the said morpholinium or thiomorpholinium derivatives at an earlier stage in the process by which cellulose is converted to regenerated cellulose, preferably in the preparation of the refined chemical pulp itself, prior to any of the steps normally associated with the viscose process. The compounds which are incorporated into refined chemical pulp in accordance with the present invention conform to the generic formula



wherein,

X=a radical selected from the group consisting of oxygen, sulfur, sulfoxide, and sulfone,

R=an aliphatic hydrocarbon group containing from 1 to 24 carbon atoms, the three R's may be different hydrocarbon groups within said limit, and the total number of carbon atoms in the three R's being from 8 to 26.

Compounds of this type can be prepared by the methods of Niederl and his associates as described, for example, in J. A. C. S. 63, 1476; 66, 840; 67, 1227; 68, 714; 70, 618. The morpholine derivatives are preferably made from dichlorodiethyl ether, a primary aliphatic amine containing a 6 to 24 carbon atom chain, and a dialkyl sulfate. The thiomorpholine (also called thiamorpholine) derivatives are preferably made by substituting dichloro-diethyl sulfide (mustard gas) for the ether in the morpholine reaction, while the sulfoxides and sulfones can be obtained by first oxidizing the mustard gas to the desired state.

Examples of compounds of this group are hexyl-methyl-morpholinium methosulfate; octyl-ethyl-morpholinium methosulfate; lauryl-methyl-morpholinium methosulfate; cetyl-methyl-morpholinium methosulfate; lauryl-methyl-mor-

pholinium ethosulfate; lauryl-ethyl-morpholinium ethosulfate; hexyl-methyl-thiomorpholinium methosulfate; lauryl-methyl-thiomorpholinium methosulfate; cetyl-ethyl-thiomorpholinium ethosulfate; lauryl-methyl-1-oxythiomorpholinium methosulfate; lauryl-methyl-1-dioxythiomorpholinium methosulfate, octadecyl-ethyl-morpholinium ethosulfate, octadecenyl-ethyl-morpholinium ethosulfate and octadecadienyl-ethyl-morpholinium ethosulfate.

Of the class of compounds defined by formula and exemplified above, preferred members are N,N di-aliphatic-hydrocarbon-radical substituted morpholinium alkylsulfates wherein one of said hydrocarbon radicals contains from 12 to 18 carbon atoms and the other of said hydrocarbon radicals is an alkyl radical with not more than 2 carbon atoms, and wherein the alkyl sulfate radical contains not more than 2 carbon atoms. All of the compounds exhibit stability in strong alkaline media such as is employed in converting cellulose to alkali cellulose, in xanthating solution, in weaker alkaline media such as viscose solution, and in acid solution such as is employed in the coagulating or regenerating bath.

Because of their unique combination of stability, solubility in all of the viscose processing solution, and high substantivity for cellulose fibers the compounds herein described stay with the cellulose through all of the stages of viscose manufacture when incorporated with the refined cellulose pulp. When the cellulose is in solution to be filtered free of dust, gel clumps, and the like, the said compounds are not removed since they are soluble. When solution is being expressed from cellulose fibers as in the preparation of alkali cellulose, the said compounds are strongly adsorbed on the cellulose fibers and the separated liquid is virtually free therefrom.

The presence of the morpholinium and thiomorpholinium compounds is beneficial in several of the steps of the viscose process and harmful in none of them; accordingly, I incorporate them with the cellulose at an early stage in the process, preferably during the course of preparing the cellulose pulp itself. Being surface active, the said compounds aid in the penetration of the fibrous masses of cellulose by the various treating solutions improving uniformity of reaction between the fibers and the said solutions. This has the indirect effect of improving the ease of filtration of the completed viscose solution because the number of suspended unreacted fibers and gel clumps of partially processed fibers is minimized. And, finally, the prevention of encrustation of extrusion orifices in the final regeneration step as taught in my hereinbefore mentioned application is effected.

In practicing the invention, a small proportion, as for example, from 0.01 to 0.2% of the surface active compound is incorporated with the cellulose in any suitable manner. In view of the hereinbefore disclosed tendency for the compounds of the invention to be strongly adsorbed by cellulose fibers the incorporation may conveniently be effected by dissolving the appropriate amount of said compound in the water used in washing the pulp subsequent to digestion of the wood chips in the sulfite process. Alternatively, relatively concentrated aqueous solutions of the said compounds may be sprayed on formed sheets of refined cellulose pulp after they have been partially dewatered but before they are dried.

Example I

Inject into the stream of washing water in the washing of refined pulp a 10% aqueous solution of N-methyl-N-lauryl morpholinium methosulfate until one pound of such solution has been injected per hundred pounds of dry cellulose fiber in the batch being washed.

Example II

Apply a uniform spray of a 20% aqueous solution of N-ethyl-N-cetyl-morpholinium ethosulfate to a wet web of refined cellulose pulp at the rate of 10 lbs. solution to 100 lbs. of dry cellulose in the web and dry the said web.

The invention is not to be taken as limited to the specific illustrations given, but is of more general application as will be apparent to those skilled in the art. It should be pointed out that it is not essential to employ pure chemical compounds as the surface active addition agents, since equally valuable results are obtained using mixtures prepared by adding together different pure compounds of the class described, or mixtures occurring as the result of using mixed reactants (such as commercial grades of amines) in the manufacture of the morpholinium and/or thiomorpholinium derivatives. By way of example a preferred morpholinium compound for use in the present invention may be obtained by alkylating with diethyl sulfate the condensation product of dichlorodiethyl ether with a mixture of aliphatic amines containing approximately 10% hexadecylamine, 10% octadecyl amine, 35% octadecenyl amine, and 45% octadecadienyl amine. The said mixture of aliphatic amines is that obtained by converting the carboxyl (—COOH) radical of soya acids to the aminomethyl (—CH_2NH_2) radical (Armeen SD of Armour and Co.), and for convenience the morpholinium derivative may be termed N-ethyl-N-soya hydrocarbon-morpholinium ethosulfate.

What is claimed is:

1. As a composition of matter, refined cellulose pulp having incorporated therein a minor proportion of an N,N-dialiphatic-hydrocarbon-radical substituted morpholinium alkyl sulfate, wherein one of said hydrocarbon radicals contains from 12 to 18 carbon atoms and the other of said hydrocarbon radicals is an alkyl radical with not more than 2 carbon atoms, and wherein the alkyl sulfate radical contains not more than 2 carbon atoms.

2. As a composition of matter, refined cellulose pulp having incorporated therein a minor proportion of N-methyl-N-lauryl-morpholinium methosulfate.

3. As a composition of matter, refined cellulose pulp having incorporated therein a minor proportion of N-ethyl-N-cetyl-morpholinium ethosulfate.

4. As a composition of matter, refined cellulose pulp having incorporated therein a minor proportion of N-ethyl-N-soya-hydrocarbon-morpholinium ethosulfate.

5. As a composition of matter, refined cellulose pulp having incorporated therein from 0.01 to 0.2% of a compound as defined in claim 1.

6. As a composition of matter, refined cellulose pulp having incorporated therein from 0.01 to 0.2% of N-methyl-N-lauryl-morpholinium methosulfate.

7. As a composition of matter, refined cellulose pulp having incorporated therein from 0.01 to 0.2% of N-ethyl-N-cetyl-morpholinium ethosulfate.

8. As a composition of matter, refined cellulose pulp having incorporated therein from 0.01 to 0.2% of N-ethyl-N-soya hydrocarbon-morpholinium ethosulfate.

9. In the viscose process for producing regenerated cellulose, the improvement which consists in introducing to the process, with the refined cellulose pulp and prior to conversion of the said pulp to alkali cellulose, a minor proportion, based on the said cellulose pulp of an N,N-di-aliphatic-hydrocarbon-radical substituted morpholinium alkyl sulfate, wherein one of said hydrocarbon radicals contains from 12 to 18 carbon atoms and the other of said hydrocarbon radicals is an alkyl radical with not more than 2 carbon atoms, and wherein the alkyl sulfate radical contains not more than 2 carbon atoms.

10. The process improvement of claim 9 wherein the said substituted morpholinium alkyl sulphate is N-methyl-N-lauryl-morpholinium methosulfate.

11. The process improvement of claim 9 wherein the said substituted morpholinium alkyl sulphate is N-ethyl-N-cetyl-morpholinium ethosulfate.

12. The process improvement of claim 9 wherein the said substituted morpholinium alkyl sulphate is N-ethyl-N-soya hydrocarbon-morpholinium ethosulfate.

13. In the viscose process for producing regenerated cellulose the improvement which consists in introducing to the process with the refined cellulose pulp and prior to conversion of the said pulp to alkali cellulose, from 0.01 to 0.2%, based on the refined cellulose pulp, of N-methyl-N-lauryl-morpholinium methosulfate.

14. In the viscose process for producing regenerated cellulose the improvement which consists in introducing to the process with the refined cellulose pulp and prior to conversion of the said pulp to alkali cellulose, from 0.01 to 0.2%, based on the refined cellulose pulp, of N-ethyl-N-cetyl-morpholinium ethosulfate.

15. In the viscose process for producing regenerated cellulose the improvement which consists in introducing to the process with the refined cellulose pulp and prior to conversion of said pulp to alkali cellulose, from 0.01 to 0.2% based on the refined cellulose pulp, of N-ethyl-N-soya hydrocarbon-morpholinium ethosulfate.

KENNETH R. BROWN.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,417,992	Niederl	Mar. 22, 1947
2,432,127	Schlosser et al.	Dec. 9, 1947
2,495,833	Brown	Jan. 31, 1950