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TREATMENT OF ACID SETTING BATHS USED IN THE MANUFACTURE OF CELLULOSE PRODUCTS FROM VISCOSE

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The present invention relates to a new and improved composition of acid setting baths utilized in the manufacture of cellulose products from viscose, and is more especially concerned with an improved process for the separation by flotation of sulfur from the acid setting solution employed, for example, in the manufacture of artificial silk in accordance with the viscose wet spinning process.

In accordance with the invention, applicants provide a novel composition of an acid setting bath which they have discovered to be very favorable to the flotation of sulfur therefrom, and which is at the same time not deleterious to the manufacturing process in any way.

More specifically, applicants have made the discovery that certain classes of wetting agents selected for their sulphur wetting powers and for their stability and solubility in acid when employed in the acid setting solution in a special range of concentrations, provide ideal reagents to be added to the acid setting baths for the flotation of sulphur therefrom.

By "wetting agents" is meant a class of surface active compounds comprising one or more hydrocarbon groups connected to a water solubilizing polar group in such a manner that the resulting structure possesses hydrophilic-hydrophobic balance, and has the property of lowering the surface tension of water and aqueous solutions when added thereto, thus enabling the production of froth by the means usual to the flotation art. The terms hydrophilic and hydrophobic are used to define the functions of the respective parts of the compounds employed in the practice of the applicants' invention, and are used in the sense generally understood in physico-chemical terminology as exemplified in Wetting and Detergency, published by the Chemical Publishing Co. of New York, 1939.

The hydrophilic polar group in the several compounds included within the applicants' invention, as hereinafter more fully described, will consist of the basic nitrogen atom as present in the examples of ammonia, amino and amido compounds listed, the sulphuric and sulphonic acid radicals as present in the examples of the substituted sulphate and sulphonate compounds listed, and the polyhydroxy and polyether groups in the examples of the substituted glycol and polyglycol condensation products listed. The hydrophobic portions of the several compounds referred to are the hydrocarbon substitution groups contained therein consisting of aliphatic, aromatic or substituted aromatic hydrocarbon groups of from five to eighteen carbon atoms.

Over a wide range of concentrations, such compounds could be expected to, and actually do behave as non-collecting frothers, in water and aqueous solutions, and are therefore of themselves not regarded essentially as flotation agents.

Contrary to expectations, applicants have found that certain wetting agents of the general type described, when added to the fouled setting solution in the proper concentrations, have a powerful action as collecting frothers to separate out the sulfur, and further that the inclusion of such wetting agents in the composition of the acid setting solution within the range of concentrations herein specified, has no deleterious effects whatever on the spinning process.

The invention will more readily be understood from the following examples.

Example I

(*a*) Three kilograms of typical rayon spinning bath containing approximately 10 percent of sulfuric acid, 18 percent of sodium sulfate, 2 percent of zinc sulfate, and heavily fouled with suspended sulfur were treated in a laboratory model Fagergren flotation machine with .001% (by weight) of dodecyl trimethyl ammonium bromide. The froth was quite manageable and a very satisfactory clarification was obtained in 2 minutes.

(*b*) A second experiment was performed similar in all respects to the first except that only .0002% (by weight) of dodecyl trimethyl ammonium bromide were used. The froth was very low and the clarification obtained in 2 minutes was only slight.

(*c*) A third experiment was performed similar in all respects to the preceding except that .008% (by weight) of dodecyl trimethyl ammonium bromide were used. In this case the froth was very high and quite unmanageable, carrying so much of the original charge that no separation was effected.

Example II

Three kilograms of typical spinning bath of approximately the same composition as set forth in Example I were treated with approximately .0006% (by weight) of a dodecyl polyglycol ether. The froth was fairly low and well-mineralized and a quite satisfactory clarification was obtained in 2 minutes.

In general, applicants have found greater sulfur collecting powers are possessed by those surface active compounds which contain the hydrophobic group in that portion of the molecule which yields the positive ion. Example I is illustrative of a substance from this group. It will be understood that the invention is not limited to the compound mentioned, but includes other compounds of similar structure and nature, of which the surface active portion thereof is a positive ion containing one radical of not less than 5 carbon atoms. Representative of this group of compounds are the following: dodecyl amido ammonium sulfate, cetyl dimethyl ammonium bro-

mide, cetyl trimethyl ammonium bromide, octadecyl trimethyl ammonium bromide.

From experiment I which is representative of many such experiments which have been performed, it is concluded that dodecyl trimethyl ammonium bromide and similar compounds of this group, when used in concentrations ranging between .0001% and .01% by weight, are extremely effective as flotation agents for the removal of sulfur from spin bath. As the concentration of the substance is decreased toward and beyond the lower limit suggested of .0001%, the effectiveness of the substance to effect flotation of sulfur from the acid setting solution rapidly diminishes. Within the range above suggested, and particularly in the middle portion thereof, as exemplified by Example I, part *a*, a most rapid and effective flotation of sulfur was effected. As the concentration of the substance is increased toward and beyond the upper limit suggested of .01%, the frothing becomes much greater, and the property of the substance as a collector disappears.

Surface active compounds which contain the hydrophobic group in the negatively charged portion of the molecule or anion, when added to acid setting solution in concentrations ranging between .0001% and .01%, have been found to exhibit strong frothing powers and sulfur collecting ability, but are markedly inferior to the first group in the latter respect. These substances may, however, be employed with advantage for the flotation of sulfur from acid setting solutions. The following compounds may be mentioned as representative of this group: sodium dodecyl sulfate, sodium tetrahydro-napthalene sulfonate, monobutyl diphenyl sodium monosulfonate, sodium isobutyl naphthalene sulfonate, and mixtures of such surface active compounds containing sodium dodecyl sulfate and free dodecyl alcohol, added as such, or resulting from hydrolysis of the former, with or without pine oil. Such compounds will also include any sulphonic acid of a petroleum hydrocarbon containing from 6 to 16 carbon atoms or its sodium salt.

A third group of compounds also possessing characteristic hydrophilic-hydrophobic balance, but are not generally considered ionogenic, possesses marked sulfur collecting powers coupled with frothing ability of moderate strength as exemplified by Experiment II. In this group is included compounds comprising an aliphatic chain of 8 to 18 carbon atoms connected to a polyhydroxy and/or a polyether nucleus of hydrophilic character, such as mono-octyl ether of diethylene glycol, dodecyl ether of sorbitol or of alkoxy sorbitol and dodecyl polyglycol ether.

Applicants' discovery that surface active materials of the general class described may be employed in certain concentrations in the composition of acid setting solutions for the removal of sulfur from the fouled solution by froth flotation, constitutes an important advance in the art, both in point of efficiency of the clarifying process, and in point of availability of such a process for use under prevailing commercial conditions. The recovery of sulfur obtained has been found to be more complete and much more rapid than in the case of reagents previously employed. These substances have been found ideal, in that they have boiling points so high that there is little or no tendency for evaporation when the setting solution is passed through the usual vacuum evaporators. Loss of the reagent from the solution due to evaporation is therefore substantially prevented, and replacement reduced to a minimum. Furthermore, these substances have been found to be extremely stable in solution, so that there is no tendency toward the giving off of any fumes or odors which could produce deleterious effects on the mill operatives. These substances have the further advantage that in the extremely small concentrations employed, no deleterious effects can be detected either in the effective composition of the bath or in the viscose coagulating or spinning operation associated therewith.

The use of certain groups of surface active compounds possessing characteristic hydrophylic-hydrophobic balance in accordance with the invention, including such compounds which contain the hydrophylic group in the negatively charged portion of the molecule, and such compounds which are generally not considered ionogenic, form the subject-matter of a copending application of the present inventors, Serial No. 502,296, filed September 14, 1943, for Treatment of acid setting baths used in the manufacture of cellulose products from viscose.

The invention having been described, what is claimed is:

1. A method of clarifying fouled regenerating baths from the regeneration of hydrated cellulose from viscose, which bath contains sulfur deposited out of solution, which comprises subjecting the bath to froth flotation by passing an inert gas upwardly through the bath in the presence of an aliphatic-group substituted ammonium compound having from 5 to 18 carbon atoms in a concentration optimum for the flotation of sulfur formed as a by-product in the bath, and removing the froth which contains the bulk of the turbid impurities.

2. A method of clarifying fouled regenerating baths from the regeneration of hydrated cellulose from viscose, which bath contains sulfur deposited out of solution, which comprises subjecting the bath to froth flotation by passing an inert gas upwardly through the bath in the presence of dodecyl trimethyl ammonium bromide in a concentration range between .0001% to .01% by weight, and removing the froth which contains the bulk of the turbid impurities.

3. A method of clarifying fouled regenerating baths from the regeneration of hydrated cellulose from viscose, which bath contains sulfur deposited out of solution, which comprises subjecting the bath to froth flotation by passing an inert gas upwardly through the bath in the presence of dodecyl amido ammonium sulfate in a concentration range between .001% and .01% by weight, and removing the froth which contains the bulk of the turbid impurities.

4. A method of clarifying fouled regenerating baths from the regeneration of hydrated cellulose from viscose, which bath contains sulfur deposited out of solution, which comprises subjecting the bath to froth flotation by passing an inert gas upwardly through the bath in the presence of octadecyl trimethyl ammonium bromide in a concentration range between .0001% and .01% by weight, and removing the froth which contains the bulk of the turbid impurities.

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