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PREPARATION OF A STABLE CELLULOSE
NITRATE HAVING GOOD ADHESIVE CHARACTERISTICS

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1

This invention relates to the imparting of adhesive characteristics to cellulose nitrate by acting thereon with a solution of H_2SO_4 in an inert diluent.

Cellulose nitrate ordinarily is prepared by reacting on cellulose with a mixture of nitric and sulfuric acids, followed by centrifuging and washing with hot water to remove the acids therefrom, as described, for example, in U. S. Patent No. 2,118,275 of Talbot. The resulting nitrated cellulose is, however, characterized by mediocre adhesive characteristics in many applications.

One object of our invention is to provide a method of treating cellulose nitrates to improve their adhesive characteristics. Another object of our invention is to prepare stable sulfate containing cellulose nitrates. Other objects will appear herein.

We have found that cellulose nitrates such as are ordinarily adapted for sheeting or the like, when treated for a short time with sulfuric acid in a diluent, acquire adhesive characteristics making those products useful in any situation where good adhesiveness is desirable. We have found that the treatment of cellulose nitrate with H_2SO_4 in a diluent results in imparting thereto a sulfate content within the range of 0.3%-3% which is obtained in accordance with our process in a stable condition.

Our invention involves treating cellulose nitrate such as that having a nitrogen content of 10-12% nitrogen and a viscosity (A. S. T. M.) of 2-80 seconds with sulfuric acid in a diluent which does not gelatinize the nitrocellulose or cause it to lose its structure.

We have found that sulfuric acid concentrations within the range of 10-30% have been the most suitable in preparing products in accordance with our invention. If a proportion of sulfuric acid much higher than 30% is employed, the product which is obtained thereby may be of such a nature that stabilization thereof would be difficult. Consequently, too concentrated sulfuric acid solutions are to be avoided. On the other hand, with concentrations of sulfuric acid much below 10% the adhesive properties which are imparted to the cellulose nitrate are too slight to warrant the treating of the cellulose nitrate therewith.

The diluents employed in our processes should be miscible with sulfuric acid and, yet, should be sufficiently non-solvent of the cellulose nitrate or the product obtained that its fibrous nature is not deteriorated or destroyed. We have

2

found that any liquid which exhibits these characteristics may be employed, water having been found to be particularly good for use as a diluent in our process. We have found, however, that a mixture of aliphatic alcohol of at least four carbon atoms, which is miscible with sulfuric acid, with a petroleum distillate or some other inert liquid miscible therewith may be employed in such proportion that its miscibility with sulfuric acid is not affected. The petroleum distillate or other inert organic liquid is preferably employed in an amount in excess of its miscibility with the alcohol such as 10-30% more, as a matter of economy. If the treating bath is allowed to stand it will, as a result, separate into two layers. The petroleum distillates which have been found to be useful mixed with the aliphatic alcohols for this purpose are those having a boiling point within the range of 80-125° C. Instead of petroleum distillates other liquid hydrocarbons such as toluene, for example, may be employed in this connection. The criterion as to the value of the liquid mixture is its miscibility with sulfuric acid and its inertness to the fibrous structure of the cellulose material. Any liquid having these characteristics may be employed as a diluent in preparing cellulose esters having good adhesive characteristics as described herein.

After the reaction of the cellulose nitrate with the sulfuric acid it is desirable to subject it to a further treatment to render the product more stable. This can be accomplished by soaking the product in a dilute solution of an alkali metal hydroxide or an alkali metal salt of a weak acid. Some of the stabilizing alkalies which may be employed for this purpose are sodium hydroxide, sodium carbonate, sodium acetate, sodium borate, trisodium phosphate, sodium oxalate, or the like. The diluted alkali which is employed to treat the product should be of a strength of at least 0.01% but insufficient to discolor the cellulose derivative prepared in accordance with our invention.

Thus, the concentration of stabilizing agent will be varied according to the strength of that alkaline material. For instance, if sodium hydroxide is used as the stabilizing agent in the form of its solution in alcohol, it should not be employed in a concentration much more than 0.05% to avoid formation of color. If an aqueous solution of NaOH is used for stabilizing any concentration up to 0.5% may be employed without discoloration of the product or causing any substantial viscosity reduction. With sodium acetate, on the other hand, a concentration of

3

1% thereof may be employed for the stabilizing procedure, while with sodium carbonate and sodium borate concentrations of approximately 4% may be employed. The concentrations given for the solutions of the various alkalis for stabilizing the cellulose derivative are fairly close to the permissible maximum and the alkali strength used should be near those given. If desired, lesser concentrations of alkali may be employed and a stabilizing effect will be obtained governed by the alkali strength and concentration which is used. The most favorable concentration of the alkaline material is that which is just short of the value which will cause discoloration of the product.

In the treatment of the cellulose nitrate with sulfuric acid the time of treatment will vary depending upon the conditions employed. For instance, with diluents which have a softening effect on the cellulose nitrate such as butyl alcohol-hydrocarbon the treatment will take place in less than an hour. On the other hand, if a diluent such as water is employed, it may even be an advantage to first soften the starting material such as by means of soaking in a pre-treating reagent such as 3% sodium hydroxide for a time. Also, the diluent employed in the stabilizing treatment may be a factor in variation of the time thereof which is employed from one case to the next. This treatment may vary from the product in alkali metal hydroxide for a few minutes up to the use of the alkali metal salt of a weak acid for a much longer time.

The following examples illustrate our invention:

Example 1.—A dry nitrocellulose having a nitrogen content of 11% and an A. S. T. M. solution viscosity of 40 seconds was soaked over night in a .3% solution of sodium hydroxide. The mass was then washed and was placed in a bath consisting of a 20% aqueous solution of sulfuric acid, the mass having the following composition:

450 parts of nitrocellulose (dry weight)
200 parts of H_2SO_4 (95%)
798 parts of tap water and
2 parts of nitric acid, the nitric acid having been added to inhibit corrosion of equipment.

The starting nitrocellulose was used water wet, the water content having been taken into account in computing the required amounts of sulfuric acid and water for the treatment. The mass was heated to a temperature of 120° F. and was allowed to remain for two hours whereupon it was cooled to 70° F. and the acid was centrifuged therefrom. The product was washed with cold tap water and was then placed in a 1% aqueous solution of sodium acetate for one hour. The product which was obtained had the following analysis:

Nitrogen	10.81%
Solution viscosity	21 sec. A. S. T. M.
Sulfate content	1.06%
German heat stability	28 minutes litmus color change

Example 2.—Nitrocellulose having a nitrogen content of 11% and an A. S. T. M. solution viscosity of 16 seconds was reacted upon in a bath prepared by mixing 95% sulfuric acid with N-butyl alcohol, this mixing being done by slowly adding the sulfuric acid to the butyl alcohol with strong agitation and external cooling. The nitrocellulose employed was dehydrated and used in that condition, the butyl alcohol contained in the

4

nitrocellulose being figured in the parts of reactants present. The following quantities were used:

443 parts of nitrocellulose (dry weight)
1015 parts of 95% sulfuric acid
1969 parts of n-butyl alcohol
3680 parts of Stoddard solvent

The liquids after mixing together were brought to a temperature of 75° F. and the dehydrated nitrocellulose was introduced. Moderate stirring was employed and the nitrocellulose was allowed to remain in the mixture for thirty minutes. The mass was then centrifuged and washed with butyl alcohol, and the material was then placed in a butyl alcohol solution containing 0.05% sodium hydroxide for thirty minutes at 75° F., following which it was again washed with butyl alcohol. The product of this treatment had the following analysis:

Nitrogen	10.98%
Solution viscosity	14.5 sec. A. S. T. M.
Sulfate content	1.00%
German heat stability	28 minutes litmus color change

The products prepared in accordance with our invention may be employed wherever adhesiveness is wanted. For instance, when dissolved in an organic solvent such as acetone or ethyl alcohol, they are useful as a film cement in the editing of photographic films. The products in accordance with our invention are adapted for use in situations in which the adherence of one layer to another is not satisfactory. By applying to one of these layers a thin coating of the product as described herein before applying the second layer ordinarily good adhesiveness is obtained as the cellulose derivatives prepared in accordance with our invention are of wide application in situations of this type. As these products are soluble in methyl or ethyl alcohol, acetone, or other commonly used organic solvents, they are readily adaptable to coating on the surface of various types of film base or other sheeting.

We claim:

1. A method of preparing a stable cellulose nitrate having good adhesive characteristics which comprises heating cellulose nitrate having a 10-12% nitrogen content and 2-80 seconds viscosity with a 10-30% solution of sulfuric acid in a diluent until 0.3-3% sulfate content is imparted thereto, removing the liquid from the cellulose nitrate and then soaking it in a solution of at least .01% concentration of an alkaline material, selected from the group consisting of the alkali metal hydroxides and the alkali metal salts of weak acids for a time sufficient to impart good stability to the cellulose ester.

2. A method of preparing a stable cellulose nitrate having good adhesive characteristics which comprises heating cellulose nitrate having a 10-12% nitrogen content and a viscosity of 2-80 seconds with a 10-30% solution of sulfuric acid in water until a 0.3-3% sulfate content is imparted thereto, removing the liquid from the cellulose nitrate and then soaking it in a solution of at least .01% concentration of an alkaline material, selected from the group consisting of the alkali metal hydroxides and the alkali metal salts of weak acids for a time sufficient to impart good stability to the cellulose ester.

3. A method of preparing a stable cellulose nitrate having good adhesive characteristics which comprises heating cellulose nitrate having

5

a 10-12% nitrogen content and a viscosity of 2-80 seconds with a 10-30% solution of sulfuric acid in an inert diluent consisting of a mixture of a liquid aliphatic alcohol of at least 4 carbon atoms and a liquid hydrocarbon until 0.3-3% sulfate content is imparted to the cellulose nitrate, removing the liquid therefrom and then soaking the cellulose nitrate in a solution of at least .01% concentration of an alkaline material selected from the group consisting of the alkali metal hydroxides and the alkali metal salts of weak acids for a time sufficient to impart good stability to the cellulose ester.

4. A method of preparing a stable cellulose nitrate having good adhesive characteristics which comprises heating cellulose nitrate having a 10-12% nitrogen content and a viscosity of 2-80 seconds with a 10-30% solution of sulfuric acid in an inert diluent consisting of butyl alcohol and a petroleum distillate, boiling within the range of 80-125° C. until 0.3-3% sulfate content is imparted to the cellulose nitrate, removing the liquid therefrom and then soaking the cellulose nitrate in a solution of at least .01% concentration of an alkaline material selected from the alkali metal hydroxides and the alkali metal salts of weak acids for a time sufficient to impart good stability to the cellulose ester.

5. A method of preparing a stable cellulose nitrate having good adhesive characteristics which comprises heating cellulose nitrate having a 10-12% nitrogen content and a viscosity of 2-80 seconds with a 20% aqueous solution of sulfuric acid until a 0.3-3% sulfate content is imparted to the cellulose nitrate, removing the liquid therefrom and then soaking the cellulose nitrate in a solution of approximately 1% of sodium ace-

6

tate for a time sufficient to impart good stability to the cellulose ester.

6. A method of preparing a stable cellulose nitrate having good adhesive characteristics which comprises heating cellulose nitrate having a 10-12% nitrogen content and a viscosity of 2-80 seconds with a 20% aqueous solution of sulfuric acid until 0.3-3% sulfate content is imparted to the cellulose nitrate, removing the liquid therefrom and then soaking the cellulose nitrate in a solution of sodium hydroxide of approximately 0.05% concentration for a time sufficient to impart good stability to the cellulose ester.

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