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PREPARATION OF NONCORROSIVE ORGANIC DERIVATIVES OF CELLULOSE

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This invention relates to the treatment of organic derivatives of cellulose, such as the organic esters of cellulose, to remove therefrom or to make inactive, corrosive compounds or compounds that cause the organic derivatives of cellulose to have a corrosive effect on metallic surfaces. The treated organic derivatives of cellulose may be formed into filaments, films and molded articles without appreciably corroding the spinning jets or other metallic surfaces contacted by solutions of the organic derivative of cellulose.

An object of the invention is the economic and expeditious production of organic derivatives of cellulose that, when dissolved in a solvent, form solutions that are less corrosive than similar solutions formed of untreated organic derivatives of cellulose. Other objects of the invention will appear from the following detailed description.

In the production of organic derivatives of cellulose there are produced various compounds that are either corrosive to metals or, when an organic derivative of cellulose is dissolved in a solvent therefor, cause the formation of compounds that are corrosive to metals. Examples of one type of such compounds are those containing sulphur. These compounds prior to this invention were separated from the derivatives of cellulose, if at all, only by elaborate and involved treatments. By employing this invention, however, organic esters of cellulose either before, during or after being stabilized, are treated with an agent that tends to produce corrosive compounds. The treatment with the agent is simple and inexpensive. The treatment in accordance with this invention is carried out to such an extent as to produce an organic derivative of cellulose that is substantially non-corrosive and is completed in a short period of time.

Organic derivatives of cellulose treated in accordance with this invention may be spun into filaments by extruding the same through jets into a solidifying medium. The organic derivative of cellulose so treated does not attack the metal surrounding the orifice. When the metal of the spinning jet is attacked, the size of the orifice is enlarged or particles of the corroded metal wedged in the orifice, thus producing filaments of undesired denier. Furthermore, since organic derivatives of cellulose treated in accordance with this invention do not attack metal parts contacted thereby, they do not pick up metallic salts which tend to discolor articles formed therefrom.

In accordance with this invention we treat precipitated or solid organic derivatives of cellulose, preferably at elevated temperatures, with a dilute solution of an oxidizing agent, for example, sodium hypochlorite, peroxide, etc. After this treatment, the derivative of cellulose may be washed substantially free of the treating compound and/or the reaction products formed by same. The organic derivative of cellulose may be treated before, concurrently or after stabilizing with the oxidizing agent. The organic derivative of cellulose thus treated, when dissolved in a solvent therefor, forms a solution which is substantially non-corrosive.

This invention is especially applicable to the treatment of any organic esters of cellulose such as cellulose acetate, cellulose formate, cellulose propionate and cellulose butyrate made by processes which tend to produce corrosive materials. It is also applicable, with obvious modifications, to the treatment of nitrocellulose, cellulose ethers and mixed esters and ethers of cellulose. Examples of cellulose ethers are ethyl cellulose, methyl cellulose and benzyl cellulose.

The organic esters of cellulose that lend themselves to this invention may be made by any of the methods now employed to make the same. For example, cellulose (cotton linters, cotton, wood pulp, etc.) with or without a pretreatment in organic acid such as acetic acid and formic acid, is esterified by treating the same with an acid anhydride in the presence of an acid solvent and a catalyst. In place of the acid solvent or in connection therewith there may be used suspension liquids such as benzol. The acid solvent may be a concentrated acid corresponding to the anhydride employed, or it may be, as is preferred, glacial acetic acid. Examples of catalysts are sulphuric acid, phosphorous acid, hydrochloric acid, zinc chloride and mixtures of these.

After esterification, sufficient water may be added to convert any remaining anhydride to the corresponding acid and the mixture hydrolyzed or ripened until the desired solubility characteristics are developed. The catalyst is then neutralized and water or other non-solvent for the ester added to precipitate the ester. During this precipitation step, the ester may, if desired, be treated with a solution of a hypochlorite or other chlorine-liberating compound to bleach the same. The ester is then separated and washed free of the acid solution. The cellulose ester may then be stabilized by treating with boiling water containing small amounts of mineral acid or with steam with or without pressure. Although sta-

bilized, the ester may contain compounds which, when the ester is in solution, cause the solution to corrode or attack metals.

We have found that, if the ester is treated after the precipitation, but prior to stabilizing, by soaking the ester in a dilute aqueous solution of an oxidizing agent, the resulting ester is substantially free of the compounds, the exact chemical structure of which is unknown, that cause the ester or solutions thereof to have a corrosive effect on metals. We have also found that these undesirable compounds may be removed or diminished to below an effective quantity by soaking the stabilized ester in a dilute solution of an oxidizing agent, or adding an oxidizing agent to the stabilizing bath. The treatment of the stabilized ester is preferable as it is in general more effective and has less tendency to alter the viscosity and solubility characteristics of the ester.

The treating liquid or bath may be formed by dissolving any suitable oxidizing agent in an aqueous medium. The oxidizing agent may be, for example, sodium hypochlorite, potassium hypochlorite, ammonium hypochlorite, peroxide, sodium peroxide, and the like compounds. When treating the organic ester of cellulose, the percentage of the oxidizing agent in the treating bath should be small enough so that there is substantially no saponification of the ester due to the oxidizing agent or compounds formed from same during the treatment. The amount of the aqueous solution of the oxidizing agent is preferably from 4 to 20 or more times the weight of the derivative of cellulose, the concentration of the aqueous solution being such that the amount of the alkaline compound used is between 0.03 to 1% on the weight of the derivative of cellulose employed, and is preferably from .1 to 0.5%. We have found it is preferable to treat the organic derivative of cellulose with the oxidizing agent in a bath maintained at elevated temperature, for instance, from 50 to 100° C. It has been found most desirable to maintain the temperature of the treating bath at from 80° C. to the boiling point of the bath. The duration of the treatment may be from less than 1 to 6 or more hours. Although an elevated temperature is preferred, effective results may be obtained at room temperature by prolonging the time of treatment.

To further describe the invention and not as a limitation, the following examples are given:

Example I

Precipitated unstabilized cellulose acetate, after being washed to neutral state, is boiled four hours in an aqueous bath containing from .3 to .4% on the weight of the cellulose acetate of hydrogen peroxide. Stabilizing the ester is then carried out in the same bath with the addition of a sufficient quantity of sulphuric acid. The cellulose acetate is then washed substantially free of any oxidizing agent, dried and dissolved in acetone. The resulting solution is found to be substantially free of any corrosive compounds.

Example II

Precipitated cellulose acetate, after being stabilized and washed to neutral state is boiled for four hours in an aqueous bath containing sufficient sodium hypochlorite to produce .136% on the weight of the cellulose acetate of chlorine. The bath is approximately 20 times the weight of the cellulose acetate. The cellulose acetate is then washed substantially free of any corrosive compounds.

It is to be understood that the foregoing detailed description is merely given by way of illustration and that many variations may be made therein without departing from the spirit of our invention.

Having described our invention, what we desire to secure by Letters Patent is:

1. Method of reducing the corrosive properties of a derivative of cellulose without substantially altering the viscosity and solubility characteristics thereof, which comprises treating a stabilized derivative of cellulose with a solution containing from 0.03 to 1%, based on the weight of the derivative of cellulose present, of an oxidizing agent selected from the group consisting of sodium hypochlorite, potassium hypochlorite, ammonium hypochlorite, peroxide and sodium peroxide.

2. Method of reducing the corrosive properties of an organic acid ester of cellulose without substantially altering the viscosity and solubility characteristics thereof, which comprises treating a stabilized organic acid ester of cellulose with a solution containing from 0.03 to 1%, based on the weight of the organic acid ester of cellulose present, of an oxidizing agent selected from the group consisting of sodium hypochlorite, potassium hypochlorite, ammonium hypochlorite, peroxide and sodium peroxide.

3. Method of reducing the corrosive properties of cellulose acetate without substantially altering the viscosity and solubility characteristics thereof, which comprises treating a stabilized cellulose acetate with a solution containing from 0.03 to 1%, based on the weight of the cellulose acetate present, of an oxidizing agent selected from the group consisting of sodium hypochlorite, potassium hypochlorite, ammonium hypochlorite, peroxide and sodium peroxide.

4. Method of reducing the corrosive properties of an organic acid ester of cellulose without substantially altering the viscosity and solubility characteristics thereof, which comprises treating a stabilized organic acid ester of cellulose with an aqueous solution containing from 0.03 to 1%, based on the weight of the organic acid ester of cellulose present, of sodium hypochlorite.

5. Method of reducing the corrosive properties of cellulose acetate without substantially altering the viscosity and solubility characteristics thereof, which comprises treating a stabilized cellulose acetate with an aqueous solution containing from 0.03 to 1%, based on the weight of the cellulose acetate present, of sodium hypochlorite.

6. Method of reducing the corrosive properties of cellulose acetate without substantially altering the viscosity and solubility characteristics thereof, which comprises treating a stabilized cellulose acetate with an aqueous solution containing from 0.03 to 1%, based on the weight of the cellulose acetate present, of hydrogen peroxide.

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