Patented Jan. 18, 1938 2,105,570

# UNITED STATES PATENT OFFICE

2,105,570

## TREATMENT OF ORGANIC DERIVATIVES OF CELLULOSE

William Whitehead, Cumberland, Md., assignor to Celanese Corporation of America, a corporation of Delaware

No Drawing. Application September 30, 1936, Serial No. 103,397

10 Claims. (Cl. 260—102)

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 so 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 derivatives 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 either as labile sulphur bodies or the less labile sulphur bodies of a higher degree of oxidation. These corrosive bodies also form with the metals insoluble compounds or compounds which are less readily dispersed and are less stable when dispersed, and further these bodies undergo changes, both physical and chemical, resulting in agglomeration, chokage of filters, lining jet orifices, etc. 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 remove corrosive compounds, or compounds which tend to produce corrosive compounds. 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 noncorrosive and is completed in a short period of time. The treatment in accordance with this invention also increases the stability of cellulose esters to ageing and heat.

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 are 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 I treat precipitated or solid organic derivatives of cellulose, preferably at elevated temperatures, with a dilute solution of oxalic acid. After this treatment, the derivatives of cellulose may be washed substantially free of the oxalic acid and/or the reaction products formed by same. If desired the organic derivatives of cellulose, after treatment with oxalic acid, may be drained and dried leaving at least a trace of the oxalic acid in the organic derivatives of cellulose. The organic derivatives of cellulose may be treated before or after a treatment with the oxalic acid with chlorine or a chlorine-liberating compound such as sodium hypochlorite. An organic derivative of cellulose thus treated, when dissolved in a solvent therefor, forms a solution which is substantially noncorrosive.

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 that are formed by processes which tend to produce corrosive materials. It is also applicable in an obvious way to the treatment of corrosive 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, hydrochlorite 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 hydrolized 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 stabilized, the ester may contain compounds which, when the ester is in solution, cause the solution to corrode or attack metals.

I have found that, if the ester is treated after precipitation, but prior to stabilizing, by soaking the ester in a dilute aqueous solution of oxalic acid, the resulting ester is substantially free of compounds, the exact chemical structure of which is unknown, that cause the ester or solutions thereof to have a corrosive effect on metals. I 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 oxalic acid. The latter method of treating stabilized esters is preferable as it is in general more effective and has less tendency to alter the viscosity and solubility characteristics of the ester. The soaking treatment is preferably carried on at elevated temperature, for instance, at from 50 to 100° C. Although soaking a precipitated derivative of cellulose in a dilute solution of oxalic acid is a preferred method, other methods may be employed such as spraying said solution on the derivative of cellulose or working the derivative of cellulose in a countercurrent manner in a stream of said solution.

The treating liquid or bath may be formed by dissolving a suitable quantity of oxalic acid in water. When treating organic esters of cellulose, the percentage of oxalic acid in the treating bath should be so regulated that there is present in the bath from between 0.03 to 1% of oxalic acid on the weight of the organic ester of cellulose being treated. The amount of the aqueous solution of oxalic acid is preferably from 4 to 20 or more times the weight of the derivative of cellulose. Although the treating bath may be of any suitable temperature, for instance, from 50° to 100° C., it has been found preferable to maintain the temperature at from 80° C. to the boiling point of the bath. The length of time required to treat a batch of the organic esters of cellulose will depend somewhat upon the original corrosive properties of same and upon the temperature and concentration of the oxalic acid solution. In general, soaking the organic ester of cellulose from 1 to 5 hours at or near the boiling point of the bath has been found sufficient.

The treatment of the derivative of cellulose with the aqueous solution of oxalic acid may be preceded or followed by a treatment with an alkaline hypochlorite. The alkaline hypochlorite treatment is not absolutely necessary. The treatment with the oxalic acid solution is sufficient to form non-corrosive derivatives of cellulose where it is undesirable to use thereon chlorine bleaching agents.

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 for 4 hours in an aqueous bath containing 0.03% on the weight of the cellulose acetate of oxalic acid. The bath is approximately 20 times the weight of the cellulose acetate. The treating bath is drained from the cellulose acetate and the cellulose acetate stabilized in a normal manner, washed, dried and dissolved in a suitable solvent. The resulting solution is found to be substantially free of any corrosive compounds.

*Example II*

Precipitated stabilized cellulose acetate, after being washed to neutral state, is boiled for four hours in an aqueous bath containing 0.04% on the weight of the cellulose acetate of oxalic acid. The bath is approximately 20 times the weight of the cellulose acetate. The cellulose acetate is washed, dried and dissolved in a suitable solvent. The resulting solution is found to be substantially free of any corrosive compounds with a much reduced $SO_4$ content.

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

Having described my invention, what I desire to secure by Letters Patent is:

1. Method of reducing the corrosive properties of a derivative of cellulose, which comprises treating a stabilized derivative of cellulose with oxalic acid for a period of at least one hour.

2. Method of reducing the corrosive properties of an organic ester of cellulose, which comprises treating a stabilized organic ester of cellulose with oxalic acid for a period of at least one hour.

3. Method of reducing the corrosive properties of cellulose acetate, which comprises treating a stabilized cellulose acetate with oxalic acid for a period of at least one hour.

4. Method of reducing the corrosive properties of an organic ester of cellulose, which comprises treating a stabilized organic ester of cellulose with a dilute solution of oxalic acid for a period of at least one hour.

5. Method of reducing the corrosive properties of cellulose acetate, which comprises treating a stabilized cellulose acetate with a dilute solution of oxalic acid for a period of at least one hour.

6. Method of reducing the corrosive properties of cellulose acetate, which comprises treating a stabilized cellulose acetate with a dilute aqueous solution of oxalic acid for a period of at least one hour.

7. Method of reducing the corrosive properties of an organic ester of cellulose, which comprises treating at elevated temperatures a stabilized organic ester of cellulose with oxalic acid for a period of at least one hour.

8. Method of reducing the corrosive properties of an organic ester of cellulose, which comprises treating a stabilized organic ester of cellulose with a boiling solution of oxalic acid for a period of at least one hour.

9. Method of reducing the corrosive properties of cellulose acetate, which comprises treating a stabilized cellulose acetate with an aqueous solution containing from 0.03 to 1.0%, based on the weight of the cellulose acetate present, of oxalic acid for a period of at least one hour.

10. Method of reducing the corrosive properties of cellulose acetate, which comprises treating at elevated temperatures a stabilized cellulose acetate with an aqueous solution containing from 0.03 to 1.0%, based on the weight of the cellulose acetate present, of oxalic acid for a period of at least one hour.

WILLIAM WHITEHEAD.