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TREATMENT OF DERIVATIVES OF CELLULOSE

George Schneider, Montclair, N. J., assignor to Celanese Corporation of America, a corporation of Delaware

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This invention relates to derivatives of cellulose and relates more particularly to the treatment of organic derivatives of cellulose to reduce their corrosive properties and color and increase their clarity characteristics.

An object of my invention is to treat derivatives of cellulose, particularly organic derivatives of cellulose, with bleaching agents to improve their properties. Another object of my invention is to treat organic derivatives of cellulose with solutions of hypochlorites whereby the corrosive properties of the organic derivative of cellulose are reduced. Other objects of the invention will appear from the following detailed description.

Organic derivatives of cellulose, such as cellulose acetate, as ordinarily made contain certain colored constituents or ingredients that tend to impair their usefulness in the making of plastics, films, filaments and the like, particularly where transparency and freedom from color are desired. Thus, when a thick sheet or block of a plastic composition containing such derivatives of cellulose is made, the same has a distinct greenish brown color and is of poor transparency.

Organic derivatives of cellulose, such as cellulose acetate, as ordinarily made also contain certain constituents or ingredients that tend to corrode metallic machine elements and parts of filament-spinning and plastic-working devices. For instance, in spinning a solution of cellulose acetate dissolved in a volatile solvent by extruding the same through suitable orifices into an evaporative or precipitating medium, the solutions containing the cellulose acetate as normally made tend to corrode the jet holes or orifices. If the corroded material remains in the jet hole, there is produced a filament having a denier below that desired, while if the corroded material is broken away from the jet hole the jet hole is enlarged, thus producing a filament having a greater denier than that desired and of undesirable cross-section. It has been the practice heretofore to frequently change the spinning jets and to make periodic examination as to their condition. This interrupts spinning. Moreover, jet replacements are costly. Furthermore, if improper inspection is made or the jets are not replaced frequently there is produced a yarn which is not uniform as to denier, cross-section, etc. This non-uniformity of the yarn reflects in the fabric produced from the same, sometimes making a second quality fabric.

I have found that if derivatives of cellulose, and particularly organic derivatives of cellulose, are subjected to the action of a hypochlorite, chlorine water or other bleaching agent prior to being precipitated from the solution in which they are formed, a large proportion of the color imparting and corrosive constituents are either destroyed or are converted into compounds that tend to produce such objectionable action to a lesser extent.

In accordance with my invention, I prepare derivatives of cellulose of reduced corrosive properties and of reduced color which derivatives of cellulose are capable of producing products of greater transparency, by subjecting the primary, secondary or working solution of the organic derivative of cellulose to the action of a bleaching agent comprising a hypochlorite, chlorine water or other chlorine liberating material. Chlorine gas may also be employed as the corrosion reducing agent.

While other derivatives of cellulose, such as cellulose nitrate, may be treated in accordance with this invention, I prefer to treat organic derivatives of cellulose, such as organic esters of cellulose and cellulose ethers. Examples of organic esters of cellulose are cellulose acetate, cellulose formate, cellulose propionate and cellulose butyrate, while examples of cellulose ethers are ethyl cellulose, methyl cellulose and benzyl cellulose.

The organic derivative of cellulose may be formed by any suitable method. For instance, cellulose acetate may be formed by treating cellulose with acetic anhydride in the presence of a catalyst and a suitable diluent or solvent such as acetic acid. The cellulose acetate thus formed may be subjected to a hydrolysis or ripening treatment to produce the desired solubility characteristics therein. The ripening or hydrolysis may be performed by allowing the cellulose acetate still dissolved in the liquors formed during esterification to stand for a period of time at suitable temperatures. By this process cellulose acetate which when formed is soluble in chloroform may be made soluble in acetone. The other esters of cellulose may be formed in a similar manner. For the purpose of describing this invention and in the appended claims, the term "primary solution" refers to a solution of cellulose ester in the solvent produced or added during the esterification of the cellulose. For instance, the primary solution of cellulose acetate as formed in accordance with the above description, is the acetic acid solution of cellulose acetate containing some acetic anhydride and sulphuric acid. Also for the purpose of describing this invention and in the appended claims, the term "secondary solution" refers to a solution of cellulose ester in the solvent produced or added during the hydrolysis or ripening. Further, for the purpose of describing this invention and in the appended claims, the term "working solution" refers to a solution of a cellulose ester, or other organic derivative of cellulose, after it has been precipitated from the primary or secondary solution, stabilized and redissolved in a solvent from which it will be formed into an article.

Although I have found that satisfactory results may be obtained by treating the derivatives of cellulose with a solution of a hypochlorite by adding the same to the esterification mixture before or during the hydrolysis and ripening steps, I prefer to treat the derivatives of cellulose at the end of the hydrolysis or ripening step. Thus, the secondary solution of cellulose acetate may have added thereto a hypochlorite solution immediately prior to or during the precipitation of the cellulose acetate from the solution. The precipitating step may be effected by adding to the secondary solution of cellulose acetate a solution of an alkali carbonate or an alkali acetate or other alkali salt of a fatty acid in a quantity sufficient to neutralize the catalyst, then adding water until the material is precipitated and the inorganic salts formed are washed out. It is during this step that I prefer to subject the cellulose acetate to the action of a hypochlorite. The hypochlorite solution may be added to the secondary solution prior to the addition of the alkali carbonate or acetate, or the hypochlorite solution may be added concurrently therewith. However, the hypochlorite solution should be added before the addition of the large amount of water used in precipitating the cellulose acetate. In like manner, the other organic esters and ethers of cellulose may be subjected to the hypochlorite treatment.

Any suitable hypochlorite may be employed in my invention, examples of which are the hypochlorites of sodium, potassium, calcium or magnesium. The hypochlorite is applied preferably in an aqueous solution and of suitable concentration, and the time of treatment is as required, say from 1 minute to 3 hours or more, depending on the concentration of the hypochlorite solution, the relative action of the same on the cellulose derivative and the condition of and chemicals contained in the primary solution of the cellulose derivative. In order to effect a rapid and high degree of bleaching, the temperature of the treatment may be raised to above that of room temperature, say from 24 to 100° C. However, this is not necessary and successful results are obtained even at temperatures below room temperature.

Cellulose derivatives, having been treated with a hypochlorite solution at the end of the ripening or hydrolysis period and then precipitated, may be given a second hypochlorite treatment if desired. This latter treatment tends to form a derivative of cellulose which is more clear, particularly when formed into a sheet or block, while the first treatment with the hypochlorite of the cellulose derivative in its primary or secondary solution tends to greatly reduce the corrosive properties of the material.

The derivatives of cellulose, when treated by my process, forms plastics, yarns and the like of greater brilliancy, clarity and freedom of color than may be made by an untreated cellulose. It is eminently suitable for making clear plastics that have no pigments or dyes or for the making of light colored plastics. However, the derivative of cellulose produced by my process may be employed for making dark colored materials.

The derivative of cellulose, when treated by my process, may be formed into sheets and films by casting the same on film-forming wheels and belts formed of metal alloys without corroding the same. Films formed of a corrosive derivative of cellulose tend to take on a color or absorb the discolored products of corrosion from the film-casting belt or wheel. This property is obviated from the derivative of cellulose produced in accordance with my invention, and a solution of such derivatives of cellulose in a volatile solvent therefor may be spun into filaments through spinning jets made of metal alloys with substantially no corrosive action on the spinning jets. Thus, a cellulose derivative produced in accordance with my invention forms more uniformed filaments, yarns, straws, etc. than those made of untreated derivatives of cellulose. The spinning into filaments or yarns of an organic derivative of cellulose, treated in accordance with my invention, is also more economical than the spinning of untreated derivatives of cellulose in that the periods of inspection of the jet orifice may be less frequent and the replacing of jets substantially eliminated.

The derivatives of cellulose treated in accordance with my invention may also be associated with volatile solvents therefor, and also plasticizers such as triacetin, diethyl tartrate, dibutyl tartrate, diethyl phthalate, triphenyl phosphate, etc. by any known processes, to form plastic sheets, blocks, tubes, rods or articles by any suitable process. Another important application of this invention is in the making of molding powders containing a purified derivative of cellulose in finely divided condition in association with plasticizers but containing little or substantially no volatile solvents, which molding powders may be molded under heat and pressure to the desired shape. Films to be employed as a base for photographic or cinematographic films or for other purposes may also be made from this material. The purified derivative of cellulose may also be used for making lacquers, particularly clear or light colored lacquers. The derivatives of cellulose made in accordance with this invention, being substantially non-corrosive, are particularly suitable for use where solutions of the same in volatile solvents are used to repeatedly or continuously contact with the same metal surfaces.

Although it is preferable to treat the derivative of cellulose with the hypochlorite solution at or near the end of the hydrolysis or ripening period, such solutions nevertheless may be treated with the hypochlorite solution immediately after esterification or etherification. For instance, cellulose acetate may be treated while in the chloroform-soluble state immediately after the cellulose has been esterified by acetic anhydride and prior to any substantial ripening or hydrolysis.

In order further to illustrate my invention, but without being limited thereto, the following specific examples are given:

Example I

Cellulose acetate is formed by the acetylation of cellulose with acetic anhydride in the presence of glacial acetic acid as a solvent and a suitable catalyst such as sulphuric acid. The solution formed after acetylation is allowed to stand at a temperature which produces a ripening or hydrolysis and thereby imparts thereto the desired solubility characteristics. After the desired solubility characteristics are obtained, a 20% aqueous solution of sodium acetate is whipped into the solution to neutralize the sulphuric acid catalyst. The solution may then be treated by subjecting the same to a solution of hypochlorite, the proportions as follows:

To every 100 parts (dry weight) of cellulose acetate dissolved in the acetic acid of the secondary solution there is added 5 parts by weight of a 12.1% aqueous solution of commercial calcium hypochlorite. The hypochlorite solution is thoroughly whipped or stirred into the cellulose acetate solution. The cellulose acetate may then be precipitated from the solution by adding thereto, preferably while constantly agitating the same, a large quantity of water, for instance, 800 parts by weight of water. Other methods of performing the precipitation may be employed. The cellulose acetate after the treatment with the hypochlorite solution and precipitation is separated from the mother liquor and the solution of hypochlorite is washed from 1 to 5 or more times until free of chlorine and is then dried.

The cellulose acetate so treated in the foregoing example has its color greatly reduced and its corrosive properties reduced substantially to a minimum.

Example II

The procedure of Example I is followed except that the solution of calcium hypochlorite is added prior to the "killing" of the catalyst with the alkali carbonate or acetate. The cellulose acetate thus produced has substantially the same properties as that produced by Example I.

Example III

The procedure of forming cellulose acetate is the same as that described in Example I except that the solution of calcium hypochlorite is mixed with the aqueous solution of sodium acetate and the solution containing the mixed salts added to the secondary solution of cellulose acetate. The cellulose acetate thus produced has substantially the same characteristics as those produced by the process of Example I.

Example IV

Cellulose acetate prepared by the process of Example I, II or III may be treated while still wet from the precipitation and washing steps with a bleaching agent preferably consisting of sodium hypochlorite in the proportions as follows:

To every 100 lbs. of cellulose acetate figured on a dry basis, there is added 0.36 gallon of 3% available chlorine aqueous solution of sodium hypochlorite in approximately 121.2 gallons of water. In place of sodium hypochlorite any other chlorite containing available chlorine or an oxidizing bleaching agent, such as peroxide, may be employed. The material thus treated may be given 1 to 5 or more washings with water to remove all traces of chlorine.

The cellulose acetate as treated in the last example is non-corrosive and has its color greatly reduced, and when made into plastics, films, lacquers, yarn and the like, as described above, produces products of greatly reduced color and increased brilliancy and transparency. When formed into filaments by extruding the same through orifices, it produces a substantially uniform filament without effecting by corrosion the diameter of the orifice.

After any of the above treatments containing a solution of a hypochlorite, the cellulose acetate may be given an anti-chlor treatment. For instance, to every 100 parts of cellulose acetate the same may be treated with .1 pound of borax dissolved in 121.2 gallons of water. The anti-chlor treatment may be effected on the cellulose acetate prior to precipitation in the processes described in Examples I to III inclusive.

The derivatives of cellulose may be formed in any suitable manner and any suitable percentages of catalyst, reacting acid or alcohol and solvents employed may be used. The amount of alkali carbonate or alkali salt of a fatty acid employed will depend upon the amount and nature of catalyst used during esterification and hydrolysis. The method of precipitating the derivative of cellulose is immaterial. However, I have found that the corrosive properties of the derivative of cellulose is greatly reduced if the same is treated with the hypochlorite solution prior to its precipitation from the secondary solution.

The quantity and strength of the hypochlorite solution employed will depend somewhat upon the amount of available chlorine contained in the salt. Although the percentages, weights, etc. given in the examples are preferred, a variation of 20% or more may be made in either direction without departing from the spirit of my invention. For instance, in Example I, instead of employing 5 parts by weight of a 12.1% aqueous solution of commercial calcium hypochlorite, there may be employed from less than 1 to 20 parts of the said solution, or the concentration of the solution may be modified.

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 action and otherwise improving the properties of an organic derivative of cellulose comprising treating the same while in the secondary solution with a solution capable of liberating chlorine.

2. Method of reducing the corrosive action and otherwise improving the properties of a derivative of cellulose comprising treating the same while in the secondary solution with a solution of hypochlorite.

3. Method of reducing the corrosive action and otherwise improving the properties of cellulose acetate comprising treating the same while in the secondary solution with a solution of hypochlorite.

4. Method of reducing the corrosive action and otherwise improving the properties of an organic derivative of cellulose comprising treating the same in its secondary solution and after hydrolysis with a solution capable of liberating chlorine.

5. Method of reducing the corrosive action and otherwise improving the properties of a derivative of cellulose comprising treating the same in its secondary solution and after hydrolysis with a solution of hypochlorite.

6. Method of reducing the corrosive action and otherwise improving the properties of cellulose acetate comprising treating the same in its secondary solution and after hydrolysis with a solution of hypochlorite.

7. Method of reducing the corrosive action and otherwise improving the properties of a deriva-

tive of cellulose comprising treating the same while in the secondary solution with a solution capable of liberating chlorine, and subjecting the derivative of cellulose to a subsequent treatment with an anti-chlor agent.

8. Method of reducing the corrosive action and otherwise improving the properties of an organic derivative of cellulose comprising treating the same while in the secondary solution with a solution capable of liberating chlorine, subjecting the derivative of cellulose to an anti-chlor agent and precipitating the organic derivative of cellulose.

9. Method of reducing the corrosive action and otherwise improving the properties of an organic derivative of cellulose comprising treating the same while dissolved in the secondary solution with a small amount of hypochlorite.

10. Method of reducing the corrosive action and otherwise improving the properties of cellulose acetate comprising treating the same while dissolved in its secondary solution with 5%, based on the weight of the cellulose acetate, of a 12.1% solution of calcium hypochlorite.

GEORGE SCHNEIDER.