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ELECTROLYTIC PROCESS FOR SIMULTANEOUSLY BLEACHING AND REMOVING METALLIC IMPURITIES FROM CELLULOSE ESTERS

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This invention relates to an electrolytic process for the purification of cellulose esters and particularly to the removal of metallic salts from cellulose acetate with simultaneous bleaching and hydrolyzing the cellulose acetate during this treatment.

Cellulose esters are usually prepared by a process which necessitates the use of acidic reagents which have a tendency to react upon the vessel in which the esterification reaction is carried out. It is moreover advisable to conduct the esterification reaction in a metallic container in order that the heat of reaction, particularly in the case of cellulose acetate, may be dissipated, otherwise the temperature would rise rapidly above 50° C. which is the maximum temperature allowable for the production of a good quality cellulose acetate as above this temperature a degraded product of little value is obtained. It, of course, is possible to use non-metallic containers but here again some means of heat control is necessary such as metallic cooling or heating coils, and their presence in the reaction mixture will result in metallic salts being formed by the acidic bodies with the resulting contamination of the first product.

In the manufacture of photographic materials it is absolutely necessary that the cellulose ester be as free as possible from all metallic occlusions. If the ester is to be used for lacquers and other commercial purposes it often is not so essential that the last traces of these materials be removed although the commercial value of an acetate is higher the less metallics substances present because of its better physical appearance.

One of the objects of the present invention is to treat cellulose esters by an electrolytic process whereby these metallic impurities are removed from the ester with a simultaneous bleaching of the product. Other objects will hereinafter appear.

We have found that by electrolyzing cellulose esters in a suitable conducting solution the dissolved metallic salts may be readily removed therefrom and incidentally the ester bleached by the reaction. The electrolytic removal of the salts partially explains, perhaps, the bleaching effect upon the product but apparently there exists some other bleaching action either by the gases given off about the electrodes or by some other, at present unexplainable, reaction which results in a product which is more highly bleached than would be expected by a simple removal of the metallic salts from it.

This electrolysis, we have found, can be advantageously conducted during the hydrolysis of the ester, and particularly so in the manufacture of cellulose acetate. The cellulose may be esterified by any of the well known esterification reactions using for example acetic anhydride, acetic acid and a suitable catalyst. The esterifying bath after the esterification consists primarily of a solution of the cellulose triacetate dissolved in acetic acid containing a small amount of unused acetic anhydride. By the addition to this reaction mixture of a small amount of an electrolyte such as, for example, hydrochloric acid dissolved in sufficient water and acetic acid to destroy the unused acetic anhydride or any suitable conducting acid or salt, the electrolysis may be readily carried on by a simple immersion into this solution of suitable electrodes.

The conductivity of an acetic acid solution is somewhat less than that of an ordinary electrolytic solution of metallic salts and also due to the presence of cellulose acetate in the solution the mobility of the ions is considerably retarded so that by the ordinary electrolytic process the reaction would be exceedingly slow. By a simple energetic stirring of the electrolyzing bath, however, this disadvantage may be readily eliminated. Any other means of increasing the conductivity of the solution may, of course, be used for example, increasing the concentration of water in the solution, keeping well in mind, however, that the hydrolysis of the cellulose acetate in the resulting solution be not affected by too great an addition. It is not essential that this electrolysis be conducted during the hydrolysis of the cellulose acetate for the result may be as readily affected by an electrolysis of the cellulose acetate in the hydrated or unhydrated form by merely dissolving such cellulose acetate in a solvent such as acetic acid and a suitable electrolyte and electrolyzing in the above described manner. This process, however, has the disadvantage that it entails a separate and distinct operation with its accompanying added expense to the process and the finished product.

When purifying esters such as cellulose nitrate the electrolysis may be conducted in a solvent or non-solvent bath of the ester with or without the addition of a conductivity increasing material.

The choice of electrodes for our electrolytic process is somewhat limited, particularly if the ester is to be used for the manufacture of photographic materials. While carbon electrodes will readily remove the metallic constituents from

a bath, nevertheless the chance sluffing off of carbon particles will render the cellulose ester product unsuited particularly for photographic purposes. We have found it advisable, therefore, that the anode be constructed of some non-corrodible material such as platinum which is not affected by any of the materials in the electrolytic bath.

If the ester is to be used for purposes other than photographic and it is not essential that the minutest quantities of such impurities as carbon be removed the carbon anode would, of course, be suitable. Other noble metal anodes or anodes constructed from non-corrodible alloys would likewise be suitable if the added expense of their use can be afforded.

The material of which the cathode is constructed is naturally of not so great importance for the reason that the metals are plated upon it and there is practically no dissolving of the metal cathode surface into the solution. The cathode surface of the common metals such as copper, iron, nickel, etc. may, therefore, be employed.

The electro potential required to carry out this electrolysis will be governed by the usual rules of electrolysis such, for example, as the distance between the electrodes and the surface area of the electrodes. The current consumption is found to be quite low as in some instances a current density of six amperes per square foot are found sufficient to completely strip a bath of the metallic salts during the time required to hydrolyze the acetate.

We shall now give an example of a preferred form for carrying out our invention but it shall be distinctly understood that we are not to be limited thereby except as is indicated in the appended claims.

Fifty parts of cellulose are pretreated in a bath containing 490 parts of acetic acid and 3½ parts of a mixed catalyst consisting of 2.6 parts of phosphoric acid, 95% strength and .9 part of sulfuric acid of 98% strength at a temperature of 38° C. for approximately 4 hours. The temperature is then lowered to about 15° C. and 150 to 170 parts of 85% acetic anhydride is added. The temperature is kept well below 42° C. and after a period of approximately 8 hours cellulose triacetate is obtained.

To this reaction mixture is added a solution containing 26.2 parts of water, 40 parts of glacial acetic acid and 2 parts of concentrated hydrochloric acid. Into this solution is placed a platinum anode and a copper cathode with a suitable stirring mechanism and a potential of 60 to 90 volts with a current density of six amperes per square foot may be applied for a period of 23 to 25 hours. The cellulose acetate will be found to be hydrolyzed to an acetone soluble product and the electrolysis will have bleached the cellulose acetate and likewise removed practically all the color due to the dissolved copper or other salts which may have been originally present.

From a consideration of the above description of our process it is evident that various electrolytic cells may be employed for conducting our electrolytic purification process, the cellulose ester may be contained in any solution from which the copper salts may be electrolyzed and any suitable type of the well known electrolytes may be added without in any way departing from our invention or sacrificing any of the advantages that may be derived therefrom.

What we claim as new and desire to secure by Letters Patent is:

1. A process for simultaneously bleaching and removing the impurities from cellulose esters, which comprises subjecting a conducting solution containing a cellulose ester to electrolysis.

2. A process for simultaneously bleaching and removing the impurities from cellulose acetate, which comprises subjecting a conducting solution containing a cellulose acetate to electrolysis.

3. A process for simultaneously bleaching and removing the impurities from cellulose acetate which comprises subjecting an acetic acid solution containing cellulose acetate to electrolysis.

4. A process for simultaneously bleaching and removing the impurities from cellulose acetate which comprises subjecting an aqueous acetic acid solution of cellulose acetate to electrolysis.

5. A process for simultaneously bleaching and removing the impurities from cellulose acetate which comprises subjecting an aqueous solution containing cellulose acetate, acetic acid and an electrolyte to electrolysis.

6. A process for simultaneously bleaching and removing the impurities from cellulose acetate which comprises subjecting an aqueous solution of acetic acid, hydrochloric acid and cellulose acetate to electrolysis.

7. A process for simultaneously bleaching and removing the impurities from cellulose acetate which comprises subjecting a conducting solution containing cellulose acetate to electrolysis during the hydrolysis of the cellulose acetate.

8. A process for simultaneously bleaching and removing the impurities from cellulose acetate which comprises subjecting an acetic acid solution containing cellulose acetate to electrolysis during the hydrolysis of the cellulose acetate.

9. A process for simultaneously bleaching and removing the impurities from cellulose acetate which comprises subjecting an aqueous acetic acid solution of cellulose acetate to electrolysis during the hydrolysis of the cellulose acetate.

10. A process for simultaneously bleaching and removing the impurities from cellulose acetate which comprises subjecting an aqueous solution containing cellulose acetate, acetic acid and an electrolyte to electrolysis during the hydrolysis of the cellulose acetate.

11. A process for simultaneously bleaching and removing the impurities from cellulose acetate which comprises removing from a conducting bath containing cellulose ester impurities which are dissolved therein, by electrolysis.

12. A process for simultaneously bleaching and removing the impurities from cellulose acetate which comprises removing from a conducting bath containing cellulose acetate impurities which are dissolved therein, by electrolysis.

13. A process for simultaneously bleaching and removing the impurities from cellulose acetate which comprises plating out of a solution containing cellulose acetate the dissolved metallic impurities by electrolysis.

14. A process for simultaneously bleaching and removing the impurities from cellulose acetate which comprises plating out of an acetic acid solution containing cellulose acetate the dissolved metallic impurities, by electrolysis.

15. A process for simultaneously bleaching and removing the impurities from cellulose acetate which comprises plating out of a solution containing water, acetic acid and cellulose acetate the dissolved metallic impurities, by electrolysis.

16. A process for simultaneously bleaching and

removing the impurities from cellulose acetate which comprises plating out of a solution containing cellulose acetate the dissolved metallic impurities during the hydrolysis of the cellulose acetate.

17. A process for simultaneously bleaching and removing the impurities from cellulose acetate which comprises plating out of a solution containing acetic acid and cellulose acetate the dissolved metallic impurities, by electrolysis during the hydrolysis of the cellulose acetate.

18. A process for simultaneously bleaching and removing the impurities from cellulose acetate which comprises plating out of an aqueous solution of acetic acid containing cellulose acetate the dissolved metallic impurities, by electrolysis during the hydrolysis of the cellulose acetate.

19. A process for simultaneously bleaching and removing the impurities from cellulose acetate which comprises adding to the acetylation reaction mixture a suitable amount of a solution containing acetic acid, water and an electrolyte, and subsequently electrolyzing the solution until the cellulose acetate is sufficiently hydrolyzed.

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