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## HYDROLYSIS OF CELLULOSE ESTERS

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The present invention relates to the hydrolysis of fully esterified esters of cellulose and especially those produced by the fibrous esterification of cellulose, by means of the mixture of a phenol and a basic nitrogen compound.

The hydrolysis or saponification of cellulose esters such as cellulose acetate to convert such esters to a compound of favorable solubility has been known in the art for a long time. For instance cellulose triacetate has been allowed to stand in aqueous acid mixtures until the acetyl content has been reduced to the desired extent and a state of acetone-solubility attained. Some experimenters have pointed out that the acids which are capable of effecting saponification of cellulose acetate have a severe action on the cellulose itself which may cause a weakening of the entire cellulose structure of the ester. We have found that any danger due to the degradation of the cellulose structure by acid hydrolysis baths is completely eliminated by the hydrolysis of the cellulose ester in our hydrolysis bath which is of an alkaline nature.

Heretofore all previous attempts to hydrolyze cellulose esters by means of alkaline baths have been failures, as the product produced by those processes has been insoluble (or poorly soluble) in acetone and the conversion of the cellulose ester usually took place with irregularity. For example some of the products formed in these prior alkaline hydrolysis processes exhibit a much greater amount of hydrolysis than other portions in the same mixture. Also in those alkaline hydrolysis processes in which caustic materials such as sodium hydroxide have been employed a weakening of the structure of the cellulose apparently takes place which is fully as great as in the case of the acid hydrolysis of cellulose esters in the presence of strong mineral acids.

We have found a method of hydrolyzing cellulose esters in an alkaline solution in which there is no apparent weakening of the cellulose structure of those esters. We have found an alkaline method of hydrolyzing cellulose acetate in which an acetone-soluble produce of good appearance and high acetone-viscosity is obtained, indicating that no breakdown of the cellulose molecule has occurred.

We have found that cellulose esters may be hydrolyzed by treating them with a phenol mixed with a basic nitrogen compound. The hydrolysis may be accomplished at a higher temperature and within a shorter time than is usually permissible in the hydrolysis of cellulose esters in which there is danger of degradation at higher

temperatures from the reagents ordinarily employed in those processes. Obviously lower temperatures together with a longer time of treatment are permissible in our hydrolysis process but such lengthening of the process is undesirable from an economic standpoint.

As mentioned before our process is applicable to cellulose esters in general such as precipitated from the reaction mixture in which they were produced, and is especially applicable to the hydrolysis of cellulose esters produced in fibrous esterification processes such as one in which carbon tetrachloride or benzene is employed as the non-solvent. Spray dried cellulose esters from which the acid has been eliminated may also be hydrolyzed by the process of our invention.

The following specific examples are illustrative of our invention and are in nowise limiting as to the scope thereof:

### Example I

25 lbs. of a cellulose triacetate resulting from the fibrous acetylation of cellulose was dissolved in 125 lbs. of phenol (Eastman white label). About 23 lbs. of a 28% aqueous ethylamine solution was then added and the mixture was placed in an oven at a temperature of 53° C. Samples were removed at intervals and the cellulose ester was separated therefrom by precipitation in hot alcohol. The resulting ester separated from the dope was washed free of phenol with alcohol, followed by washing with water, and drying. The ester from each interval was analyzed and the following results were found:

Time of treatment	Acetyl content	Solubility
Hours	Per cent	
0	44.2	Chloroform.
4	41.3	Acetone.
8	39.8	Acetone.
24	36.0	-----

The product obtained in the above example in the 4-8 hour range was found to give solutions in acetone comparable to the acetone solutions of cellulose esters resulting from the most satisfactory processes of hydrolyzing cellulose acetate known at the present time.

### Example II

To 50 lbs. of phenol was added 10 lbs. of 28% aqueous ethylamine solution and 10 lbs. of cellulose triacetate. The mixture was maintained at

about 50-55° C. for 6 hours, at the end of which time the hydrolyzed acetate was precipitated by pouring into hot alcohol. The precipitate was thoroughly washed with hot alcohol, then with hot water and then dried. The product was found to be soluble in acetone in which it gives a brilliant smooth dope of very good viscosity.

### Example III

The process in Example II was repeated except that 10 lbs. 28% aqueous ammonium hydroxide was employed instead of ethyl amine. A product equal to that produced in Example II was obtained.

The products obtained by the hydrolysis of cellulose esters are eminently suitable for the production of skins or sheeting which may be employed for making photographic film, wrapping tissue, laminated glass or any of the uses to which cellulose derivative sheeting is put at the present time. These products are also eminently suitable for the production of filaments of artificial silk, molding powders, lacquers or any use for which a pure undegraded hydrolyzed cellulose ester is suitable. The products formed by our process may be mixed with plasticizers such as triphenyl phosphate which are well-known as plasticizers for cellulose acetate. Various other plastic materials such as gums, waxes, resins, other cellulose esters etc. which are compatible with the hydrolyzed esters produced by our invention may also be incorporated with those hydrolyzed esters if desired.

Although our invention is concerned primarily with the hydrolysis of cellulose triacetate to acetone-solubility, due to the commercial importance of acetone-soluble cellulose acetate at the present time, it is also applicable to the higher esters of cellulose both simple and mixed whether or not they are originally acetone-soluble. For example cellulose butyrate or cellulose acetate-butyrate even though they be soluble in acetone may be hydrolyzed by our process to give products having properties differing from the completely esterified esters of cellulose. As disclosed in Malm and Fletcher application Serial Number 551,546 filed July 17, 1931, various mixed organic esters of cellulose when hydrolyzed give films of greater flexibility from some organic solvents than the corresponding unhydrolyzed esters so that even though the fully esterified esters may be originally acetone-soluble, the hydrolysis of such esters may be desirable.

Although the basic nitrogen compounds given in the examples were employed because of their commonness and availability, any other basic nitrogen compound which is compatible with the process of our invention may be employed. Instead of ethylamine, amines which possess some other alkyl group may be employed. The use of methyl amine is restricted to some extent due to its limited solubility in water but where this factor is immaterial it may be employed in our process as the basic nitrogen compound. Amines which contain one or more phenyl groups are also restricted as to use due to their slight solubility in water. Besides the organic derivatives of ammonia known as primary amines, the secondary and tertiary amines which have more than one alkyl (or like) group attached to the nitrogen atom may be employed in our process. Any chemical compound may be employed in our process which belongs to the class known to chemists as "the basic nitrogen compounds" and

which is physically compatible with the materials employed in the process.

Other phenols than phenol itself such as a cresol may be employed in our hydrolysis process, however due to the commonness of phenol itself, and its satisfactory behavior in our hydrolysis process, its use is preferred at the present time.

Various other modifications and variations such as in time, temperature, proportions etc. which are a matter of individual judgment and technique also come within the scope of our invention.

We claim as our invention:

1. The hydrolysis of an organic ester of cellulose in a hydrolyzing bath essentially consisting of a phenol and a basic nitrogen compound.

2. The hydrolysis of an organic ester of cellulose in a hydrolyzing bath essentially consisting of a phenol and a compound having the formula:



in which X, Y or Z, each may be either a hydrogen, alkyl or aryl group.

3. The hydrolysis of an organic ester of cellulose in a hydrolyzing bath essentially consisting of phenol and a basic nitrogen compound.

4. The hydrolysis of an organic ester of cellulose in a hydrolyzing bath essentially consisting of phenol and a compound having the formula:



in which X, Y or Z each may be either a hydrogen, alkyl or aryl group.

5. The hydrolysis of an organic ester of cellulose in a hydrolyzing bath essentially consisting of a phenol and a basic nitrogen compound containing an NH group.

6. The hydrolysis of an organic ester of cellulose in a hydrolyzing bath essentially consisting of a phenol and a basic nitrogen compound containing an NH<sub>2</sub> group.

7. The hydrolysis of a fatty acid ester of cellulose in a hydrolyzing bath essentially consisting of a phenol and a basic nitrogen compound.

8. The hydrolysis of a fatty acid ester of cellulose in a hydrolyzing bath essentially consisting of a phenol and a compound having the formula:



in which X, Y, or Z each may be either a hydrogen, alkyl or aryl group.

9. The hydrolysis of a fatty acid ester of cellulose in a hydrolyzing bath essentially consisting of phenol and a basic nitrogen compound.

10. The hydrolysis of a fatty acid ester of cellulose in a hydrolyzing bath essentially consisting of phenol and a compound having the formula:



in which X, Y or Z each may be either a hydrogen, alkyl or aryl group.

11. The hydrolysis of an organic ester of cellulose in a hydrolyzing bath essentially consisting of a phenol and an alkylamine.

12. The hydrolysis of an organic ester of cellulose in a hydrolyzing bath essentially consisting of phenol and an alkylamine.

13. The hydrolysis of cellulose acetate in a hydrolyzing bath essentially consisting of a phenol and a basic nitrogen compound.

14. The hydrolysis of celluloses acetate in a

hydrolyzing bath essentially consisting of a phenol and a compound having the formula:



drolyzing bath essentially consisting of a phenol and ethylamine.

18. The hydrolysis of cellulose acetate in a hydrolyzing bath essentially consisting of phenol and ethylamine.

19. The hydrolysis of cellulose acetate in a hydrolyzing bath essentially consisting of a phenol and ammonium hydroxide.

20. The hydrolysis of cellulose acetate in a hydrolyzing bath essentially consisting of phenol and ammonium hydroxide.

in which X, Y or Z each may be either a hydrogen, alkyl or aryl group.

15. The hydrolysis of cellulose acetate in a hydrolyzing bath essentially consisting of phenol and a basic nitrogen compound.

16. The hydrolysis of cellulose acetate in a hydrolyzing bath essentially consisting of a phenol and an alkyl amine.

17. The hydrolysis of cellulose acetate in a hydro-

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