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PROCESS OF CHANGING THE SOLUBILITY OF MIXED ESTERS OF CELLULOSE AND THE PRODUCT RESULTING THEREFROM

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This invention relates to a process of changing the solubility of the mixed organic esters of cellulose by treating them with a dilute acid bath at an elevated temperature for a predetermined period of time.

The mixed esters of cellulose have been known for several years as shown for example by British Patent No. 219,926. In spite of this knowledge of the mixed esters, however, it has not been previously recognized to our knowledge that these esters may be changed in solubility or other properties in the manner herein described so that the individual esters may be adapted to various purposes.

One object of our invention is to provide a process in which the properties of mixed organic esters of celulose may be altered in the degree desired to adapt the ester for the particular purpose for which it is to be used. Previously, fully esterified mixed cellulose esters have been known and used but the properties of the particular ester made according to a certain process could only be altered by substituting more of the radical which it is desired should influence the characteristics of the ester, than of the other radical or radicals which are joined to the cellulose. For example, a cellulose acetate-stearate in which acetyl radicals predominate will more closely resemble cellulose acetate than the same mixed ester with a large stearyl content and vice versa.

Another object of our invention is to provide a process in which any cellulose sulfo-acylate, which has been formed such as in the making of the mixed esters of celulose in the presence of sulfuric acid, may be substantially eliminated. For example, in cellulose acetate-propionate, the presence of cellulose sulfo-acetate-propionate will render the ester unstable and should be removed. By our process the undesirable sulfo containing molecules are broken up to form the stable cellulose acetate-propionate, this feature being inherent in our invention. Thus in the product of our process, liability of decomposition is eliminated.

Another object of our invention is to produce mixed organic esters which will be adapted for colloidizing, such as the forming of films or filaments, by means of solvents in which the fully esterified mixed ester itself may be insoluble. For example, a fully esterified cellulose acetate-propionate may be insoluble in a solvent composed of methyl alcohol and acetone but upon hydrolysis of such ester it becomes soluble in that mixture after a time.

Another object of our invention is to produce mixed organic esters of cellulose that will form colloidized sheets of much greater flexibility than those which can be formed from the corresponding fully esterized mixed ester by means of the same solvent.

Another object of our invention is to provide a process which makes possible a wide variation in the properties of particular mixed organic esters of cellulose, by merely varying the time and conditions of treatment. Other objects will hereinafter appear.

We have found that products with very exceptional properties can be prepared from the commonly known mixed organic esters of cellulose by replacing a portion of the acid radicals in the esters with hydroxyl groups. We have found that cellulose derivatives of predetermined characteristics may be produced by our process which admits of being easily controlled.

Our process may be used either in the case of mixed organic esters of cellulose which may be in solid form such as those produced by fibrous acetylation, or those which have been separated from their reaction mixtures such as by spray drying or precipitation, or those which are still in solution in their reaction mixtures. In the case of the employment of the esters in solid form, the process may be carried out with the ester in suspension in a hydrolyzing bath for example in an organic acid before the hydrolysis occurs. In the case of suspension hydrolysis the proportion of water or other hydrolyzing material present may as a rule be greater than that employed when the mixed ester is hydrolyzed while in solution, in an organic acid for example.

Although various known de-esterifying materials such, for example, as aqueous or alcoholic alkaline hydroxides, etc. may be employed, we prefer especially in the case of the mixed esters which are dissolved in their reaction mixture to employ water or alcohol with a mineral acid for the hydrolyzing of the esters as we have found that when those liquids are employed, the hydrolyzed mixed ester exhibits greater uniformity. To avoid precipitation of the ester from its reaction mixture the water or alcohol is usually mixed with enough organic acid such as acetic before adding to the reaction mixture so that precipitation will not occur upon such addition.

We have found that the mixed fatty acid esters of cellulose such as disclosed in U. S. Patent Nos. 1,704,282 and 1,800,860 of Clarke and Malm, are especially suited to be benefited or changed in solubility by the present process although it is

obvious to anyone skilled in the art that other mixed esters of cellulose may be changed in properties by the present process. The esters to which we have found our present process particularly applicable are cellulose acetate-propionate, cellulose propionate-butyrate, and cellulose acetate butyrate as well as the mixed esters of cellulose containing the high fatty acid radicals such as cellulose acetate-stearate, cellulose acetate-laurate, etc., namely, those prepared, for instance, in an esterification bath in which there is present available higher acid radicals in an amount at least equal to and preferably greater than the available lower acid radicals. In the case of the cellulose acetate-propionate, for instance, the proportion of propionyl to total acyl in the mixed ester is greater than 15%. As the percentage of the acyl of more than two carbon atoms based on the total acyl content increases as the hydrolysis of a mixed fatty acid ester of cellulose progresses, the ratio of acyl of two carbon atoms to the total acyl of the mixed ester over the entire period of the hydrolysis will always be at least 15%.

The mixed esters which are hydrolyzed by the present invention contain at least 15% of acyl of more than two carbon atoms based on the total acyl content of the cellulose. Unhydrolyzed mixed fatty acid esters of cellulose containing at least 15% of higher acyl based on the total acyl content are soluble in acetone.

The hydrolysis may obviously be carried out in a short time such as about 12 hours under intensive conditions such as elevated temperature, strong hydrolyzing agent, etc. We prefer, however, to hydrolyze the mixed esters over a long period of time which assures an easily controllable process and products which are suitable for colloidized materials such as film, sheeting, artificial silk, molded products, etc. By our hydrolysis of the mixed esters the "precipitation value" of the ester is kept above 85% and as a rule above 90% making any of these esters ideal for colloidizing purposes. In our hydrolysis the process may be stopped at any predetermined point at which the desired precipitation value has been reached. In the present process there is not the uncertainty as to the characteristics of the product which may be obtained at any point, as once these are determined for any given hydrolysis series, the characteristics at any particular point in the hydrolysis will be known and consequently a product of the properties desired may be obtained by selecting the proper hydrolysis period.

The precipitation value referred to is the percentage of cellulose ester which from an acetone solution thereof, will precipitate in a mixture of 40% water and 60% acetone by volume. This value may be determined by the following method:

5 gms. of the dry ester of cellulose is accurately weighed and placed in a wide mouth 12 oz. bottle. To this is added 100 cc. of acetone (99% or better) and the mixture is stirred until homogeneous. (The bottle should be closed during the stirring with a rubber stopper fitted with a shaft for the stirrer). A solution of cellulose ester in acetone, is formed, to which is added slowly from a pipette and with thorough stirring, 150 cc. of a mixture consisting of 2 parts of distilled water and 1 part acetone by volume. Care should be taken to keep the solvents and mixtures at 20° C. wherever volumes are being measured.

At the end of the acetone-water mixture, a mixture is obtained containing 40% water by volume (neglecting contraction) in which is suspended the ester which has been precipitated from its hydrolysis bath and dried. This is allowed to stand for 12 hours at 20° C. At the end of this time precipitation has reached equilibrium and proceeds no further, and during the same time settling of the precipitate occurs. 25 cc. of the clearest portion are removed with a pipette. This 25 cc. is centrifuged in stoppered bottles at high speed until the liquid is perfectly clear. Exactly 5 cc. of the clear liquid is then removed with a pipette and evaporated to dryness on a watch glass. If W is the weight of the residue in grams the precipitation value or the percentage of ester precipitated

$$=100-W\times\frac{250}{5}\times\frac{1}{5}\times 100$$

$$=100-1000W$$

Wherever precipitation value is referred to herein, it will be understood that the value arrived at by the foregoing method is intended.

As an illustration of our invention applied to a cellulose acetate-propionate the following example is given:

A fully esterified cellulose acetate propionate whose acyl content is made up of about 40% propionyl and 60% acetyl groups prepared by esterifying cellulose with a mixture of acetic anhydride, propionic acid and a catalyst, still in solution, was made up to the following composition by the addition of aqueous acetic acid:

	Pounds
Cellulose acetate-propionate	40
Propionic acid	120
Acetic acid	140
Water	15
Sulfuric acid	½

The whole was thoroughly mixed together and kept at 100° F. The cellulose acetate-propionate initially was soluble in any one of the following: acetone, methyl acetate, ethyl acetate, ethylene chloride, ethylene chloride-ethyl alcohol (1:1), propylene chloride-ethyl alcohol (4:1), B-B' dichloro-ethyl ether and B-B' dichlor-ethyl ether-ethyl alcohol (4:1). Sheets coated from an ethylene chloride solution of cellulose acetate-propionate before its hydrolysis were found to tolerate 6 folds in a modified Schopper fold-tester (a common method of determining relative flexibilities of films). After 48 hours hydrolysis, film formed from an ethylene chloride solution of the resultant cellulose acetate-propionate tolerated 7 folds on the Schopper fold-tester showing increased flexibility. After 84 hours an ester results which is soluble in butyl acetate. After 96 hours of hydrolysis, an ester results which is soluble in methyl alcohol-acetone (1:1) in addition to being soluble in butyl acetate and the solvents in which it was soluble before hydrolysis. A film coated from an ethylene chloride solution of the ester formed at this stage tolerates 9 folds on a fold-tester which was maximum flexibility for this series of cellulose acetate-propionate films coated from an ethylene chloride solution. The fold toleration of this same 96 hr. ester coated as a film from an acetone solution was 0. After 108 hours hydrolysis the cellulose acetate-propionates resulting are insoluble in butyl acetate.

The hydrolysis of cellulose acetate propionate produced as above, was carried out for 360 hours and the solubility of the ester resulting at various

stages was determined. The results were as follows:

Solvent	Solubility range (hours of hydrolysis)
Acetone	0–360
Methyl-alcohol:acetone (1:1)	96–360
(2:1)	144–360
(3:1)	180–360
Ethyl acetate	0–288
Butyl acetate	84–108
Ethylene chloride	0–168
Ethylene chloride-ethyl alcohol (4:1)	0–360
Propylene chloride-ethyl alcohol (4:1)	0–360
B-B′ dichlorethyl ether	0–144
B-B′ dichlorethyl ether-MeOH (1:1)	0–360
Benzene:ethyl alcohol (1:1)	144–360
(2:1)	144–360
Toluene:methyl alcohol (1½:1)	192–216

The flexibility of the cellulose acetate-propionate obtained in suitable stages, when colloidized, was tested on the Schopper fold-tester, referred to above, with the following results:

Time of hydrolysis (hours)	Toleration (in folds)		
	Ethylene chloride	Acetone	MeOH-acetone (1:1)
0	6		
24	6¾	0	
48	7	0	
72	7½	0	
96	9	0	
120	7½	2¾	
144		8½	7/16
156	7½	9¾	½
168		7	6
192		4½	7
216		3.7	7½
240		2½	8
264		2	7½
276		2	8½
302			8
336			8½

Over the entire hydrolysis from 0–360 hours the precipitation value was found to decrease gradually from 98% to 90%.

The hydrolysis described above reduces the total acyl content of the ester corresponding to the number of hours of hydrolysis. For instance the entire range of approximately 360 hours reduces the total acyl content of the ester to approximately 37%. The intermediate times given result in products having a total acyl content of more than 37% depending on the time employed. For instance, to obtain a total acyl content of 44.5%–41% the time necessary will be approximately 96–216 hours. To obtain a partially hydrolyzed ester of more than 44.5% total acyl content the time of hydrolysis is kept below approximately 96 hours.

A fully esterified cellulose acetate-butyrate having an acyl content made up of about 30% butyryl and 70% acetyl groups was prepared by esterifying cellulose with a mixture of acetic anhydride, butyric acid, a catalyst and a buffering agent such as sodium acetate. The resulting reaction mass was made up to the following composition by the addition of aqueous acetic acid:

	Pounds
Cellulose acetate-butyrate	50
Butyric acid	150
Acetic acid	200
Water	35
Sulfuric acid	0.5
Sodium acetate	0.1

The whole was thoroughly mixed together and was kept at 100° F. The cellulose acetate-butyrate initially was soluble in any one of the following: acetone, ethylene chloride, B-B′ dichlorethyl ether and ethyl acetate. After 96 hours' treatment of the composition at 100° F., the ester is found to be soluble in a 1:1 mixture of methyl alcohol and acetone.

The hydrolysis of the cellulose acetate-butyrate produced as described above was carried out for 360 hours and the solubility of the ester resulting at various stages was determined. The results were as follows:

Solvent	Solubility range (hours of hydrolysis at 100° F.)
Acetone	0–360
Methyl alcohol:acetone (1:1)	96–360
(2:1)	240–360
(3:1)	240–360
(4:1)	288–360
Ethylene chloride	0–288
B-B′ dichlorethyl ether	0–288
Ethyl acetate	0–288
Benzene:methyl alcohol (1:1)	240–360
(2:1)	240–360
Benzene:ethyl alcohol (1:1)	240–360
Toluene:ethyl alcohol (1:1)	312–360
(2:1)	312–360

It may be observed from the above data that by our process any desired mixed ester may be adapted to the particular solvent which it is desired to employ in colloidizing or in dissolving the ester. For example, if it is desired to coat out cellulose acetate-propionate from its solution in ethylene chloride the product from the 96 hr. stage is highly desirable from the standpoint of maximum flexibility. If acetone is the solvent preferred, the product from the 156 hr. stage will give maximum flexibility and in the case of a mixture of methyl alcohol and acetone in equal proportions, the product from the 276–336 hr. period is highly desirable. Our process also makes possible the employment of solvents for these mixed esters which heretofore have been regarded as unsuitable due to the fact that they would not dissolve fully esterified esters which were to be colloidized

It is obvious that other water-miscible organic acids than acetic acid may be employed to introduce the water into the reaction mixture for hydrolyzing the ester. For example, in the hydrolysis of cellulose acetate-propionate, aqueous propionic acid might have been employed instead of the aqueous acetic acid which was added in the example given although for economic reasons acetic acid is preferred at present.

Other catalysts instead of sulfuric acid may obviously be employed if desired. Some of the catalysts which may be employed are a phosphoric-sulfuric acid mixture (preferably 3 phosphoric:1 sulfuric), thionyl chloride, benzene sulfonic acid, toluene sulfo chloride and sodium bisulfite. The ratio of the catalytic activity of these catalysts to the mineral acids, known to the experts in the art, will give the correct proportions to employ in the particular process where it is desired to substitute them for sulfuric acid.

The mixed esters which have been hydrolyzed according to our process may then be precipitated from the hydrolysis bath by the addition of water in excess, either as such or preferably in an organic acid such as acetic acid. It is preferred that the precipitation be carried out according to Malm application No. 553,647 filed July 28, 1931, in which is disclosed the precipitation of the higher esters of cellulose in an aqueous

precipitating bath containing about 55% of an organic acid.

After the ester has been precipitated it is preferably washed and stabilized by the method disclosed in the Clarke and Clarke application No. 540,148, filed May 26, 1931 in which method the ester after washing free of acid is boiled in a purified water such as distilled water.

The hydrolysis of mixed esters of cellulose in accordance with the present invention does not reduce the total acyl content of the ester below 37%. This is an inherent property of our mixed esters when hydrolyzed for the periods herein defined or when possessed of the solubilities herein described.

Of these esters, those having an acyl content of 41–44.5% are useful for the preparation of sheeting, while those having an acyl content of more than 44.5% are of value as a lacquer base. As may be seen, for instance, from the chart on page 3, the esters having an acyl content of 41–44.5% (approximately 96–216 hours at 100° F.) exhibit good flexibility.

As pointed out previously a variety of esters may be produced by our process which are suitable for forming colloidized products such as film or sheeting, artificial silk, plastics or molded products, overcoatings, lacquers, lubricants etc. The mixed esters resulting from our process are compatible with the various commonly employed plasticizers such as triphenyl or tricresyl phosphate, etc.

Our mixed esters may be mixed with each other or with other esters of cellulose either simple or mixed. The wide range of properties which are possible with mixed esters, treated according to our process, will suggest many and various combinations and uses of these esters to those skilled in the art.

What we claim as our invention and desire to secure by Letters Patent of the United States is:

1. A process of partially de-esterifying acetone soluble cellulose acetate-propionate the acyl content of which comprises at least 15% propionyl which comprises treating it with a hydrolyzing agent and terminating the hydrolysis before the total acyl content of the acetate has been reduced to less than 37%.

2. A process of partially de-esterifying acetone soluble cellulose acetate-propionate the acyl content of which comprises at least 15% propionyl which comprises treating it with an organic acid diluted with a hydrolyzing agent and terminating the hydrolysis before the total acyl content of the acetate has been reduced to less than 37%.

3. A process of partially de-esterifying acetone soluble cellulose acetate-butyrate the acyl content of which comprises at least 15% butyryl which comprises treating it with a hydrolyzing agent and terminating the hydrolysis before the total acyl content of the acetate has been reduced to less than 37%.

4. A process of partially de-esterifying acetone soluble cellulose acetate-butyrate the acyl content of which comprises at least 15% butyryl which comprises treating it with an organic acid diluted with a hydrolyzing agent and terminating the hydrolysis before the total acyl content of the acetate has been reduced to less than 37%.

5. Partially hydrolyzed cellulose acetate propionate butyrate the acyl content of which comprises at least 15% of propionyl and butyryl groups.

6. A process of partially de-esterifying an acetone soluble mixed ester of cellulose, the acyl content of which comprises at least 15% of fatty acid radical containing more than two carbon atoms, which comprises treating it with a lower fatty acid diluted with a hydrolyzing agent and terminating the hydrolysis before the total acyl content of the acetate has been reduced to less than 37%.

7. A process of partially de-esterifying acetone soluble cellulose acetate propionate, the acyl content of which comprises at least 15% propionyl, which comprises treating with a hydrolyzing bath containing water as the hydrolyzing agent and terminating the hydrolysis before the total acyl content of the acetate has been reduced to less than 37%.

8. A process of partially de-esterifying an acetone soluble mixed ester of cellulose, the acyl content of which comprises at least 15% of higher fatty acid radical, which comprises treating it with a lower fatty acid diluted with water and terminating the hydrolysis before the total acyl content of the acetate has been reduced to less than 37%.

9. A partially hydrolyzed mixed organic ester of cellulose containing 44.5%–41% of combined acyl which combined acyl comprises at least 15% of fatty acid radicals of 3–4 carbon atoms.

10. A partially hydrolyzed cellulose acetate propionate containing 44.5%–41% of combined acyl which combined acyl comprises at least 15% of propionyl.

11. A partially hydrolyzed cellulose acetate butyrate containing 44.5%–41% of combined acyl which combined acyl comprises at least 15% of butyryl.

12. A partially hydrolyzed mixed organic ester of cellulose having a total acyl content of greater than 37%, of which at least 15% is fatty acid radical containing more than two carbon atoms.

13. Partially hydrolyzed cellulose acetate-propionate having a total acyl content greater than 37% of which at least 15% is propionyl.

14. A film or sheet containing a partially hydrolyzed mixed ester of cellulose having a total acyl content of greater than 37% of which at least 15% is fatty acid radical containing more than two carbon atoms.

15. A filament containing a partially hydrolyzed mixed ester of cellulose having a total acyl content of greater than 37% of which at least 15% is fatty acid radical containing more than two carbon atoms.

16. Partially hydrolyzed cellulose acetate-butyrate having a total acyl content of greater than 37% of which at least 15% is butyryl.

17. The process of hydrolyzing an acetone soluble mixed ester of cellulose, the acyl content of which comprises at least 15% of fatty acid radical containing more than two carbon atoms, which comprises treating it with a hydrolyzing agent and terminating the hydrolysis before the total acyl content of the ester has been reduced to less than 37%.

18. The process of hydrolyzing an acetone soluble mixed ester of cellulose, the acyl content of which comprises at least 15% of fatty acid radical containing more than two carbon atoms, which comprises treating it with an aqueous hydrolyzing agent and terminating the hydrolysis before the total acyl content of the ester has been reduced to less than 37%.

19. A partially hydrolyzed mixed organic acid

ester of cellulose having a total acyl content of more than 44.5% of which at least 15% is fatty acid radical of 3–4 carbon atoms.

20. A partially hydrolyzed cellulose acetate-propionate having a total acyl content of more than 44.5% of which at least 15% is propionyl.

21. A partially hydrolyzed cellulose acetate-butyrate having a total acyl content of more than 44.5% of combined acyl of which at least 15% is butyryl.

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