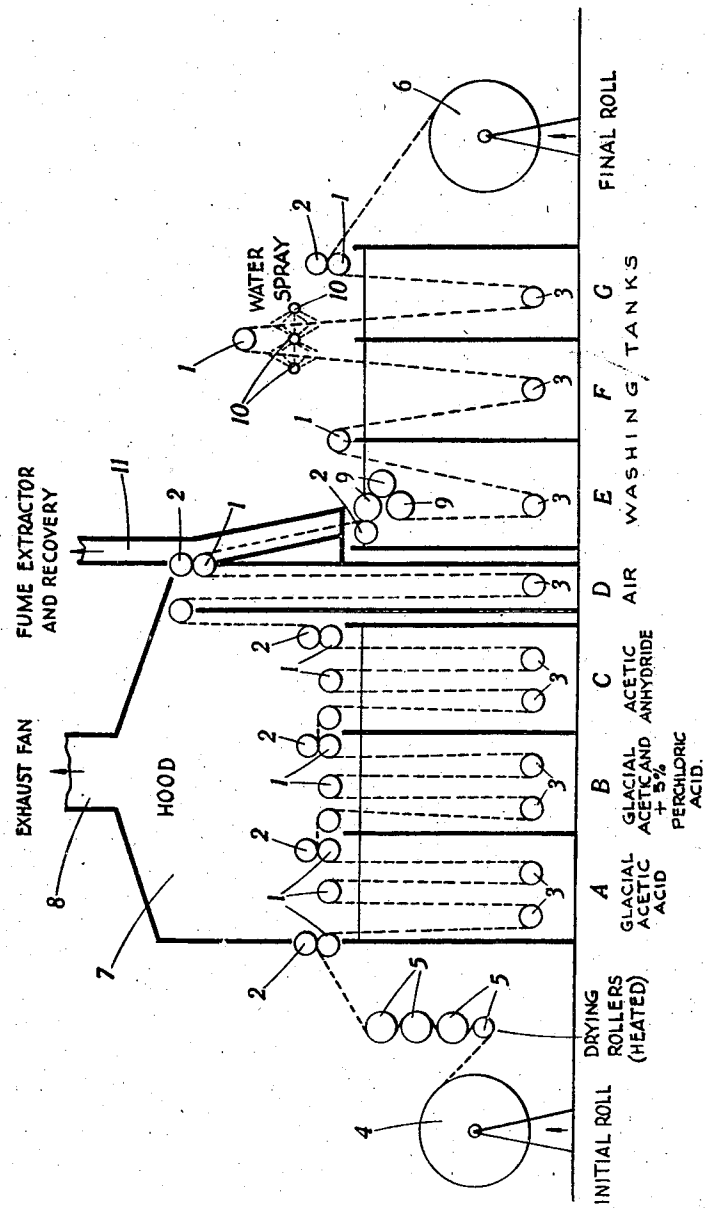
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PROCESS FOR THE ESTERIFICATION OF CELLULOSE

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PROCESS FOR THE ESTERIFICATION OF CELLULOSE

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This invention relates to a process for the esterification of cellulose to form esters of carboxylic acids having from 2–5 carbon atoms with retention of the fibrous form.

Such processes are known and have been carried out by means of a controlled esterification, that is, the process necessary for converting the cellulose into a tri-ester in solution has been carried out at a slower rate and in the presence of a non-solvent for the tri-ester, the process of esterification taking a period of some hours, even after previous soaking of the fibres for some hours in the acid, the ester of which is to be produced, and a catalyst. A comparatively mild catalyst such as zinc chloride or a salt of perchloric acid has been used.

It has also been found previously (British Patent No. 494,253) that, on carrying out a rapid esterification process of paper to form an ester of a carboxylic acid containing from 2 to 5 carbon atoms at a temperature higher than 60° C., whilst preserving the fibrous structure, the first result was an esterification of the surface layers only of the fibres, so that by carrying out the process for at least 5 minutes and for periods up to at least 20 minutes duration without pre-treatment with the acid, the tensile strength when wet was equal to that of paper having a much greater combined carboxylic acid content that had been prepared by the usual processes for uniform esterification. It is to be noted that esterified paper prepared according to this last mentioned process was not in general suitable for electric insulation purposes because of its non-uniform esterification.

The present invention comprises a process for the substantially uniform esterification of cellulose to form an ester or esters of acetic, propionic or butyric acids with retention of the fibrous form in which perchloric acid is used as a catalyst and the cellulose is passed in the form of a continuous sheet or thread through a bath or baths in which the esterification, takes place. This has been rendered possible by our discovery that perchloric acid, although a very powerful catalyst, can be used in such manner that a process of uniform esterification of cellulose, either partial or complete, can be carried out in periods that are extraordinarily brief as compared with the prior art and the fibrous structure be retained.

As an example of a process according to the invention, a sheet of 5 mil wood-pulp manila (40–60) paper (undried) is passed through a bath of glacial acetic acid to which has been added 5% by weight of commercial perchloric acid (sp. gr. 1.695) during a period of 33 seconds at room temperature and then through a bath containing 70% acetic anhydride and 30% toluene at a temperature of 49° C. for a period of 37 seconds. The sheet of paper then passes through the air at room temperature for 78 seconds and then into a washing bath of water and is afterwards dried. The paper then has a combined acetic acid content of 30%.

Paper esterified in accordance with the above example is found to be equal in electrical properties to paper esterified in accordance with known uniform esterification processes.

The exact conditions required to esterify to a given degree depend upon the particular kind of paper. For example, a denser paper requires slower running through the plant than a less dense paper to reach the same degree of esterification. A thinner paper esterifies more quickly than a thicker paper of the same grade, up to a certain degree of esterification.

The combined acetic acid content can be controlled, up to full acetylation, by the temperature of the anhydride bath. The following table shows the relation between the temperature of the anhydride bath in degrees centigrade and the combined acetic content at the conclusion of the process given in the example above, carried out upon different thicknesses of paper of the same grade, i. e. a 60% manila 40% wood pulp cable paper.

Table 1

1¾ mil.		2½ mil.		3½ mil.		5 mil.		7 mil.	
Temp.	Combined acetic acid content	Temp.	Combined acetic acid content	Temp.	Combined acetic acid content	Temp.	Combined acetic acid content	Temp.	Combined acetic acid content
°C.	*Percent*	°C.	*Percent*	°C.	*Percent*	°C.	*Percent*	°C.	*Percent*
30	18.0	30	15.8	28	11.9	30	9.0	28.5	3.8
37.5	19.8	37.5	19.2	38	12.4	40	12.5	38.0	6.9
49	23.4	51.5	27.0	50.5	22.8	48	25.0	49.0	21.4
60.5	41.9	60.5	42.5	61.0	43.8	58	40.0	60.0	45.2
65.0	54.0	65.0	54.0	70.0	58.8	70	56.0	69.5	60.0
72.5	60.0	71.5	60.0	----	--------	----	--------	----	--------

One mil. is one thousandth of an inch.

It will be observed that for lower temperatures thinner papers acetylate to a higher combined acetic acid content than thicker papers, but that at higher temperatures the reverse is sometimes the case. The above figures are generally representative of the results obtained, but owing to slight differences in different portions of a given paper, the acetylation curves on repetition will not always follow exactly the same course.

It will also be noted that between the temperatures 60–75° the acetylation speed increases until nearly maximum acetylation is reached (about 58%) after which the speed decreases rapidly.

It is to be emphasized that the process according to the invention can be carried out for all degrees of esterification up to full esterification. For many electrical purposes the improvement in insulation resistance under humid conditions obtained by carrying the process up to or beyond the di-acyl stage is not sufficiently great to be economically justified but for use as electric insulation at high frequencies, i. e. 10 kc. and above, esterification of paper as well as cotton beyond the diacyl stage is justified, since it leads to a decrease in the power factor as well as an increase in insulation resistance as compared with the same material unesterified or esterified below the di-acyl stage.

The moisture content of the original paper has an effect upon the combined acid content for a given time and temperature of reaction. In general, previous drying of the paper decreases the combined acetic acid content for a given temperature of the anhydride bath and speed of running. The following table gives the combined acetic acid contents obtained with a process according to the example mentioned above carried out upon a 2½ mil all wood cable paper, and with the same process carried out upon the same paper after it had been dried by being passed over a heated roller. Before drying the moisture content was 7%, after drying less than 1%.

Table 2

Temperature of anhydride bath	Combined acetic acid content, percent	
	Undried	Dried
20	21.5	10.0
30	27.5	16.0
40	34.0	22.2
50	40.0	28.5
60	46.0	34.8

Moreover, the product obtained from an undried paper is more even and the reaction proceeds more smoothly; the electrical properties are also slightly improved. The following table shows the transverse direct current insulation resistances of the above samples measured at 500 volts and 80% relative humidity for different combined acetic acid contents. The figures given were obtained by measurement of an area of 50 square centimeters under an applied pressure of 100 grams per sq. cm.

Table 3

Combined acetic acid content	Transverse direct current insulation resistance, megohms	
	Dried	Undried
0	268	268
10	1,000	2,500
20	6,500	7,000
30	17,800	19,600
40	50,000	100,000

The difference between the two sets of figures appears to be due to smoother acetylation taking place when water in the paper has been displaced by acetic acid. On the other hand, the treatment of undried paper by the process described in the above example leads to the weakening of the catalyst liquor. In order to retain the advantages of the treatment of undried paper without this resultant disadvantage, the paper may be passed through a bath of glacial acetic acid before passing through the glacial acetic acid plus catalyst bath. In order to retain the efficiency of dehydration it is necessary to take care that the dehydration efficiency of the acetic acid bath does not decrease unduly. We have found that below 2% of moisture in the acetic acid the efficiency of dehydration is very nearly 100%, and that it is not advisable to allow the dehydration efficiency to fall below 60%, which corresponds to a moisture content of 6.7% in the acetic acid bath. We have found that 14,500 lbs. of paper can be passed through an acetic acid bath containing 10,000 lbs. of acid before the moisture content of a paper originally containing 6% of moisture falls to 3%.

In order to avoid too frequent attention to the acetic acid dehydration bath it may be advisable to effect a preliminary drying of the paper by means of heated rollers to reduce its moisture content to 3% before passing it through the dehydration bath. The weight of paper that could then be passed through a tank containing 10,000 lbs. of acetic acid before the dehydration fails to be effective is 29,000 lbs.

The proportions of catalyst to acetic acid may be varied widely with corresponding variations in the temperatures and/or times of running through the bath for a given acetic acid content. Too great a proportion of perchloric acid, how-

ever, leads to tendering of the fibres particularly for higher degrees of acetylation. Thus 10% of perchloric acid leads to tendering of the fibres for any degree of acetylation. Assuming for purposes of comparision the times of passage through the baths given in the example previously quoted, 7% of perchloric acid may be used up to a temperature of 60° C. at which temperature 32.5% combined acetic acid content results, but at 70° C. (combined acetic acid content 47%) slight tendering takes place. Lower concentrations of catalyst than 5% may also be used and over the useful range the resultant combined acetic acid content is approximately a linear function of the concentration of catalyst. 5% of perchloric acid is the optimum value for the production of acetylated paper to a combined acetic acid content of over 10%, but for the production of very low acetylated paper, 2% is most economical.

The presence of a diluent such as toluene in the anhydride bath is not essential, and slightly higher combined acetic acid contents at the various temperatures are obtained by the use of a 100% anhydride bath, as shown by the following table of results obtained with a 60% manila 40% wood pulp 5 mil paper.

Table 4

Temperature, °C	Combined acetic acid content	
	100% anhydride	30% toluene, 70% anhydride
20	7.5	6.1
30	9.5	8.7
40	15.4	13.5
50	30.5	26.5
55	47.0	38.5
60	62.0	60.0

The presence of a diluent, however, improves the electrical properties slightly as illustrated by the following figures for the transverse direct current insulation resistance of the same paper, taken under the same conditions as for Table 3 above.

Table 5

Combined acetic acid content, percent	Transverse direct current insulation resistance in megohms	
	100% anhydride	70% anhydride, 30% toluene
0	107	107
10	350	1,100
20	1,000	9,000
30	5,500	20,000
40	10,000	45,000
50	35,000	70,000
60	50,000	100,000

The speed at which the paper is passed through the different tanks may be varied with consequent variation in the degree of esterification. A change in this speed will of course alter the other conditions, i. e. length of time during which the paper is immersed in each bath.

The following table summarises the results obtained by varying the speed. The results shown were obtained in the acetylation of paper with the use of a preliminary bath of glacial acetic acid as described above.

Table 6

Running speed in ft./min.	Immersion time in anhydride bath in secs.	Combined acetic acid content for temperature of—			
		40° C.	50° C.	60° C.	65° C.
15	10	4.0	7.0	11.0	20.0
10	15	4.5	8.0	13.5	21.5
7.5	20	6.0	11.5	17.5	25.5
6.0	25	9.5	16.5	23.0	31.0
5.0	30	14.5	22.5	31.0	39.0
4.3	35	20.0	29.5	40.5	50.0
3.75	40	27.0	38.0	60.0	
3.33	45	38.0	50.0		

It will be seen therefore that the process according to the invention is very easily controlled in order to obtain a predetermined combined acetic acid content. The speed and temperature used will depend entirely upon the paper undergoing acetylation, whether thick or thin, dense or less dense and the properties which are required from the resultant paper. The fixing of one variable automatically fixes the other for a combined acetic acid content.

The process according to the invention is applicable to the formation of cellulose esters of propionic and butyric acids. The combined acid content obtained with a given temperature and speed of passage through the various baths is lower the greater the number of carbon atoms in the acid concerned. As an illustration, a sheet of 5 mil 60% manila 40% wood pulp paper is passed through a bath of butyric acid to which has been added 5% by weight of perchloric acid (sp. gr. 1.695) during a period of 33 seconds at room temperature and then through a bath containing 70% butyric anhydride and 30% toluene for a period of 37 seconds. The temperature of this bath was varied from time to time and the portions of the sheet passed through it at the different temperatures after washing and drying tested for combined butyric acid content. In all cases, however, the sheet passed through the air at room temperature for 78 seconds to complete the reaction.

The different combined butyric acid contents are given in Table 7.

Table 7

Temperature, ° C.	Combined butyric acid content, percent
20	5
33	5.5
40	7
49	10
60	17

Thus for full esterification in the case of butyric acid the time of immersion in the anhydride bath at 60° C. would be approximately 140 secs.

It will be seen that considerable variation in the details of the process may be made. Thus in addition to variations previously noted, solvents for cellulose tri-acetate, such as acetic acid, may be added to the anhydride bath, with or without the presence of inert diluents such as toluene, benzene or the like. In some circumstances also a single bath containing acid, anhydride and catalyst, with or without a diluent may be used. It is to be noted also that the process is applicable to the formation of mixed esters of acetic, propionic or butyric acids.

It should be noted also that, although the invention is of particular value when applied to

paper as compared with known processes, since esterification of paper in roll form may give somewhat uneven results, it is equally applicable to other forms of cellulose such as cotton in the form of tapes or sheets.

In the single figure of the drawing we have shown a schematic arrangement for acetylating paper in a continuous manner. This drawing shows by way of example, a plant for the acetylation of paper in a continuous roll. The roll of paper is shown at 4. The paper is drawn from the roll 4 between drying rollers 5, which are conveniently heated by passing steam through them in well known manner. The sheet of paper then passes over and between rollers as shown through tanks A, B and C and thence through a chamber D maintained at atmospheric temperature. The paper then passes through a passage D', which is heated in any convenient manner and through washing tanks E, F and G and on to a take up roller.

The take up roller 6 and all the rollers marked 1 are positively driven. The rollers marked 2 are mounted so as to press against their corresponding rollers 1, the pressure being adjustable. The rollers marked 3 are mounted in such manner that they can be raised into position for initially passing the paper around them at the commencement of operations. The rollers 9 at the entrance to the tank E are heated and arranged after the manner of calendering rollers. Pipes 10 are arranged as shown transversely to the sheet of paper and are perforated and fed with water under pressure so that a spray of water is directed on the sheet of paper. The tanks A, B and C and chamber D are surmounted by a hood 7 having an exhaust opening 8 above which is mounted an exhaust fan (not shown). The passage D' is continued in a tube 11 which leads to a plant in which any fumes are extracted and any evaporated liquor condensed and recovered in well known manner.

The heated rollers 3 are heated to such temperature that the moisture content of the paper is reduced to 3%. The tank A contains glacial acetic acid, the tank B contains glacial acetic acid with 5% perchloric acid, and the tank C contains 70% acetic anhydride and 30% toluene. The tank C is fitted with pipes (not shown) through which steam or hot water may be circulated and pipes through which cold water may be circulated and thermostatic control means of any well known kind is provided to regulate the flow of heating and/or cooling medium through these pipes in order to keep the temperature constant at a desired figure. Stirring means (not shown) is also provided in this tank C. The tanks E, F and G are washing tanks containing water. The speed at which the take up roll 6 and the driving rollers 1 are driven is conveniently adjusted such that time of immersion in each of the tanks A, B and C is 30 seconds. The combined acetic acid content required is then controlled by controlling the temperature of the tank C as previously described.

In the machine shown the paper is wound in the wet condition on the final roll 6. The paper is then dried and it may be calendered in a separate operation. This has been found preferable since the speed of passage through the drying chamber can then be more readily controlled independently of the speed of acetylation than if acetylation, washing, drying and calendering were all performed in one continuous operation.

What is claimed is:

1. A quick, continuous process for the esterification of cellulose in continuous lengths which comprises the steps of continuously passing the cellulose through a bath of an aliphatic carboxylic acid having from two to five carbon atoms and containing 2% to 7% of perchloric acid, and then passing the thus treated cellulose continuously through a bath composed of an anhydride of an aliphatic carboxylic acid having from two to five carbon atoms.

2. A quick continuous process for esterifying cellulose in lengths which comprises continuously subjecting the cellulose length to the action of glacial acetic acid containing 2% to 7% of perchloric acid and then continuously passing the thus treated cellulose length into a bath containing acetic anhydride.

3. A quick continuous process for esterifying cellulose in lengths which comprises the steps of at least partially removing moisture from the cellulose, then continuously passing the cellulose into contact with an aliphatic carboxylic acid containing 2% to 7% of perchloric acid, and continuously passing the thus treated cellulose into contact with an anhydride of an aliphatic carboxylic acid having from two to five carbon atoms.

4. A quick continuous process for esterifying cellulose in lengths which comprises the steps of at least partially removing moisture from the cellulose, and then continuously passing the cellulose into contact with glacial acetic acid containing 2% to 7% of perchloric acid, and then continuously passing the thus treated cellulose into contact with acetic anhydride.

5. In the esterification of cellulose to form esters of carboxylic acids containing from two to five carbon atoms while retaining the tensile strength and fibrous structure of the cellulose the step which comprises subjecting the cellulose to the action of such acid and of the anhydride of such acid, at least one of such actions being in the presence of between 2% and 5% of perchloric acid.

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