HETEROGENEOUS PROCESS FOR ACETYLATION OF CELLULOSES

J. Geurden

Film Base Factory, Gevaert-Agfa N.V., Heultje, Belgium

INTRODUCTION

It is known that pretreated celluloses during their esterification dissolve in the acetylation mixture consisting of acetic anhydride, acetic acid and a catalyst. In some acetylations, this dissolution of the cellulose derivative is enhanced by the addition to the normal constituents of the acetylating mixture of a solvent for triacetate, normally methylene chloride. Since this procedure leads to à homogeneous solution of the cellulose derivative, this method of acetylation is called "homogeneous".

However, when instead of a solvent, a non-solvent for triacetate, for instance a hydrocarbon, is added to the esterifying mixture, a normal acetylation of the celluloses can nevertheless also be performed. When added in the right amount the non-solvent will prevent the dissolution of the cellulose ester and, at the end of the acetylation is found the cellulose derivative in its original fibrous structure besides the liquid reagents. This method of acetylation is called "heterogeneous".

HETEROGENEOUS PROCESS FOR CELLULOSE TRIACETATE PRODUCTION

Production method

The different steps for the production of cellulose triacetate according to the heterogeneous process are as follows.

1. The bleached cotton linters are opened by means of an opening machine. When wood pulp is used, the sheets are shredded for instance by a hammer-mill.

2. In order to obtain consistent results, and to prevent a degradation of acetic anhydride the normal moisture-content of the air-dry cellulose is reduced.

3. The celluloses are pretreated, which means that the fibres are soaked with acetic acid, or with a mixture rich in acetic acid. A simple way of pretreatment consists in dipping the celluloses in acetic acid and removing the excess of liquids, for instance, by centrifugation. Celluloses pretreated in this way have to age which means that some time has to elapse between the pretreatment and the proper acetylation.

Another method of pretreatment consists in spraying acetic acid through nozzles over and into the celluloses, and by subjecting these celluloses, during their wetting, to a mechanical work. This method, called "mechanical pretreatment" has the following advantages: (a) the ratio of pretreating agent to celluloses is predetermined and may be kept constant; (b) an increase in

the reactivity of the celluloses, an improvement of the quality of the end-product, and a reduction of the liquid retention of the aggregates of fibres resulting from the modified structure; (c) in most cases, the pretreated celluloses may be acetylated at once. When not, the ageing time may be reduced.

4. The proper acetylation of the pretreated celluloses is carried out by means of the above mentioned mixture, during which a predetermined thermal programme must be strictly followed. A uniform regulation of the temperature during this operation can be secured: (a) by mechanical stirring in a vessel, fitted with a double wall through which the cooling or heating medium flows; or (b) by circulating the acetylating mixture, which maintains its original fluidity till the end of the esterification. This circulation is effectuated by pumping the liquid during the acetylation from under the sieve-bottom, supporting the celluloses, through an external heat exchanger. After the cooling or heating the acetylating mixture flows back in the reactor. This method of acetylation is often called the "static" process.

5. When the final point of acetylation is reached, the liquids are separated from the solids. For economical reasons it is then advisable to modify after draining the composition of the liquids, retained by the fibres and still containing some acetic anhydride. This can be done (a) by centrifuging, followed or not by spraying with non-reacting liquids, e.g. a non-solvent; or (b) by a simple draining followed by displacing the residual acetylating mixture (retained by the triacetate) by means of non-reacting liquids.

6. The triacetate fibres are then subjected to the action of boiling weak aqueous acetic acid. As a result of this action the sulphoaceto cellulose, responsible for the instability of the triacetate decomposes and the cellulose ester is stabilized. This stabilization process is normally combined with the removal by steam distillation, of the non-solvents, retained by the fibres.

7. The stabilized triacetate is then rinsed with water until neutral.

8. The water content of the stabilized and neutral triacetate is reduced either by squeezing or centrifuging. Finally the triacetate is dried and baled.

The principal steps of the above procedure can also be applied in laboratory. However, in small scale acetylation it is advisable to intentionally prolong the duration of the esterification for instance by lowering the acetylation temperature. This enables a closer following of the progress of the reaction.

Disadvantages

The heterogeneous process shows the following disadvantages.

1. As far as we know, there is no existing process allowing a hydrolysis under maintenance of the fibrous form of triacetate into diacetate, with an acceptable solubility in acetone. A normal solubility of the diacetate can only be obtained by hydrolysing a dissolved triacetate, which brings us back to the homogeneous process.

2. In the heterogeneous process the esterification time is longer than in the homogeneous process.

3. As a result of the fact that the cellulose derivatives are not dissolved, the heterogeneous acetylation requires the use of larger amounts of esterifying mixture.

Advantages

On the other hand, the advantages, industrial and economical, of the heterogeneous process are:

1. In the homogeneous process the fluid reagents are converted into a viscous solution, showing a very poor heat transmission whereas in the heterogeneous process the original fluidity of the liquid reagents is maintained through the esterification. As a result thereof the temperature can be controlled, in an easy and reliable way, everywhere in the vessel, for instance by a mere recirculation of the fluid reagents. Consequently, the size of an industrial batch can be safely and substantially increased.

2. Mechanical stirring may be eliminated for the reason mentioned under 1. This means a simpler and cheaper equipment and a saving in power.

3. The non-solvent of the precooled acetylating mixture can be considered as an extra reserve of cold present exactly in those areas where as a result of the exothermic reaction heat is evolved. This reserve of cold calories counteract the ill effects of the locally evolved calories and constitutes an additional reason for easy and accurate regulation of the thermal programme.

4. As a result of the essence itself of the heterogeneous process the precipitation of the dissolved cellulose derivative, which is unavoidable in the homogeneous process, is completely superfluous. This means a saving in equipment, in time, in labour and in power. It is worthwhile to note that fibrous triacetate is easily stabilized and dried.

5. The recovery as anhydride by distillation of the acetic anhydride of the residual acetylating mixture constitutes the major advantage of this process. It is known that in the homogeneous method, the excess of anhydride—howsoever little it may be—and the acetic acid are, as a result of the precipitation, recovered as dilute acetic acid. The savings in concentration costs and reconversion costs are substantial.

LABORATORY APPLICATION OF HETEROGENEOUS METHOD

In the laboratory too, it may be useful to apply the heterogeneous process, especially when one aims at the study of the proper esterification. For at any time of the acetylation, the liquids can be separated from the partially or totally esterified fibres, by mere decantation without a precipitation being involved. This being so easy it is possible at any time of the esterification to determine: (a) Under which form and where the sulphuric acid (the catalyst normally used) is present during the esterification. (b) The amounts of combined acetic acid and combined sulphuric acid.

Analytical method for the liquids

The liquids are decanted from the solids, filtered over fritted glass, and titrated by means of 0·1 N solution of potassium acetate in anhydrous acetic acid, to which a small quantity of acetic anhydride has been added. When using methyl red as the indicator, the colour changes from red to yellow and when malachite green is the second indicator the colour changes from yellow to green. Concerning this method of titration the following remark has to be made.

In the acetic acid–acetic anhydride medium, *sulphuric acid* is titrated in the presence of the above mentioned indicators as monobasic acid, most probably because of the quasi-immediate formation of acetyl sulphuric acid in this medium. Sulpho-acetic acid in the mixture acetic acid–acetic anhydride, does not, when malachite green is the indicator, show any consumption of potassium acetate. The behaviour of toluene sulphonic acid (taken as an example of an aromatic sulphonic acid) is identical to that of sulpho-acetic acid.

The conditions become much more intricate when *mixtures of sulphuric and sulpho-acetic acids* are examined in the acetic acid acetic–anhydride medium. In this case, the total acids present are determined by titration in the presence of methyl red as well as of malachite green. Under these conditions malachite green does not indicate any difference between sulphuric acid (aceto-sulphuric acid) and sulpho-acetic acid. This ascertainment might possibly show that in this medium sulpho-acetic acid is modified and that a stronger acid is formed.

The titration of mixtures of *sulphuric acid and toluene sulphonic acid* in acetic acid–acetic anhydride determines in the presence of malachite green the sulphuric acid (acetyl-sulphuric acid) and in the presence of methyl red, the sulphuric acid and the toluene sulphonic acid. The determination becomes even more intricate in the presence of xylene, because the latter, especially at higher temperatures, is so easily sulphonated.

It seems nevertheless approximately correct to state that one titrates sulphuric acid in the presence of malachite green, and in the presence of methyl red the sulphuric acid + the aromatic sulphonic acids. When to this mixture sulpho-acetic acid is added, the latter is also titrated for the major part when malachite green is used as indicator.

Analytical method for the solids

For the determination of the combined acids, a special procedure has to be applied because the samples of the cellulose derivatives prior to drying, have to be stabilized. Owing to the formation of water-soluble cellulose derivatives during the intermediate stages of the acetylation, especially when increased amounts of catalyst are used, the usual method of stabilization, i.e. boiling the ester in very dilute acetic acid will lead to erroneous determinations. In order to avoid these the following method of stabilization was developed.

The samples taken during the esterification are washed with the normal acetylating mixture containing potassium acetate instead of sulphuric acid. After neutralization of the catalyst, the samples are washed with alcohol–water (90:10). The cellulose derivatives treated in this way can be safely dried and then subjected to the classical determination of the combined acid as for instance by the Ost-method.

EXPERIMENTAL

In the absence of celluloses

The experiment of the first series was carried out in the absence of celluloses. The following conditions were kept constant. (a) The composition of the acetylating mixture: non-solvent, 60 parts by volume; acetic anhydride, 25 parts by volume; acetic acid, 15 parts by volume. (b) The amount of catalyst, 1·5 per cent by volume. The following condition: were varied.

(i) The temperature: 0°C and 30°C; (ii) the nature of the non-solvent: benzene, toluene or xylene. At regular intervals the sulphuric acid was titrated and the results of the different titrations are presented in *Figure 1*.

On examining the results shown in *Figure 1*, in which only the results for 0° and 30°C are given, those pertaining to 15°C being intermediate, we may conclude that:

1. When using methyl red as indicator practially all results are constant, independently of the temperature and the nature of the non-solvent.

2. When using malachite green as indicator there is a continuous regression which is enhanced by an increase in the temperature and by the use of toluene or xylene instead of benzene.

The practical meaning of this reduction of the values determined in the presence of malachite green is the inactivation or "passivation" of the catalyst. This is proved by the fact that acetylating mixtures containing sulphuric acid and showing extremely low figures in the titration, do possess extremely low esterifying properties, if any, when malachite green is used as indicator and this independently of the results obtained in the
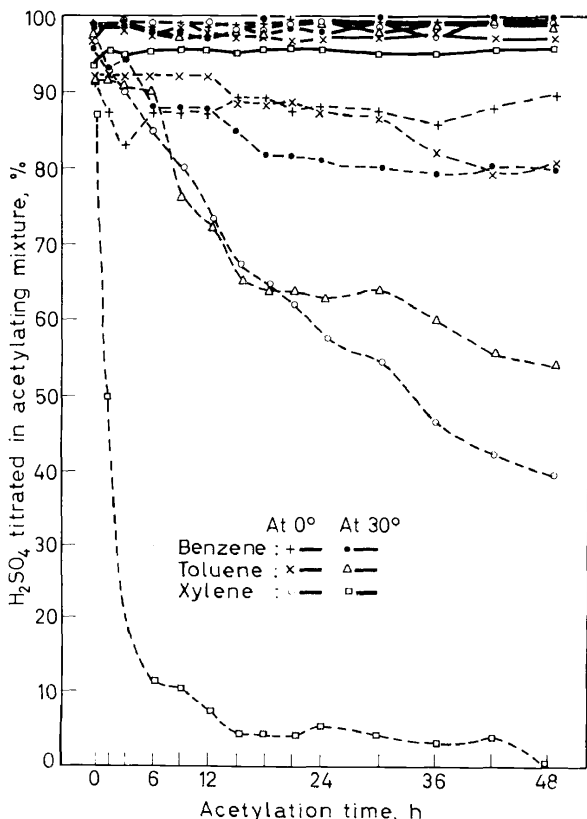

Figure 1. The amount of sulphuric acid determined in the acetylation mixture in the absence of cellulose using methyl red (full line) and malachite green (dotted line) indicators [100 per cent $H_2SO_4 = 2 \cdot 684$ g/l.]

presence of methyl red. This, of course, is only true, when sulphuric acid is not present in the fibres in some active bound form.

In the presence of pretreated celluloses

Titrations similar to those described in the case where celluloses are absent were carried out. At suitable intervals, samples were taken out of the celluloses under esterification. The amounts of combined acetic acid and sulphuric acid present in these samples were determined according to the above mentioned method. Taking into account the special affinity of sulphuric acid for the cellulose, the ratio of acetylating mixture to celluloses was kept constant during the different experiments; namely 35 parts by volume of acetylating mixture for 1 part by weight of cellulose (dry basis).

Experiment A

In this experiment the mixture consisted of (% by vol.): non-solvent (xylene), 60; acetic anhydride, 25; acetic acid, 15; and sulphuric acid, 1·5. The composition of the mixture was kept constant whereas the temperature was varied: 0°C, 5°C and 10°C. Only the results for 0°C and 10°C are given in *Figure 2*, those pertaining to 5°C being intermediate values.
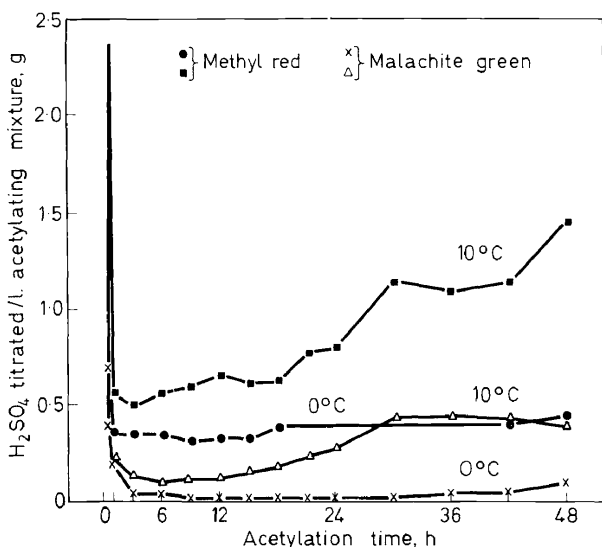

Figure 2. Effect of temperature on the acetylation of cellulose using xylene as the non-solvent and when the composition of the acetylation mixture is kept constant [composition (by volume): non-solvent (xylene), 60%; acetic anhydride, 25%; acetic acid, 15%; sulphuric acid, 1·5%]

From these results the following conclusions can be drawn. (i) The curves for methyl red and for malachite green are different, but seem to be parallel. The difference between these curves is due to a soluble form of passivated sulphuric acid not determined in the presence of malachite green. (ii) According to the temperature, the catalyst present in the mixture migrates into the cellulose fibres in the ratio of 80–98 per cent. (iii) The products

formed at 0°C may in view of their extremely low evolution be considered as permanent. (iv) At 10°C, the rapid initial fall of the catalyst present is followed by a prolonged flat-portion in the curve and subsequently by a progressive liberation of sulphuric acid.

The amount of combined acetic acid present is given in *Figure 3*. It can be seen that the esterification at 0°C proceeds slower as compared with the esterification at 10°C.
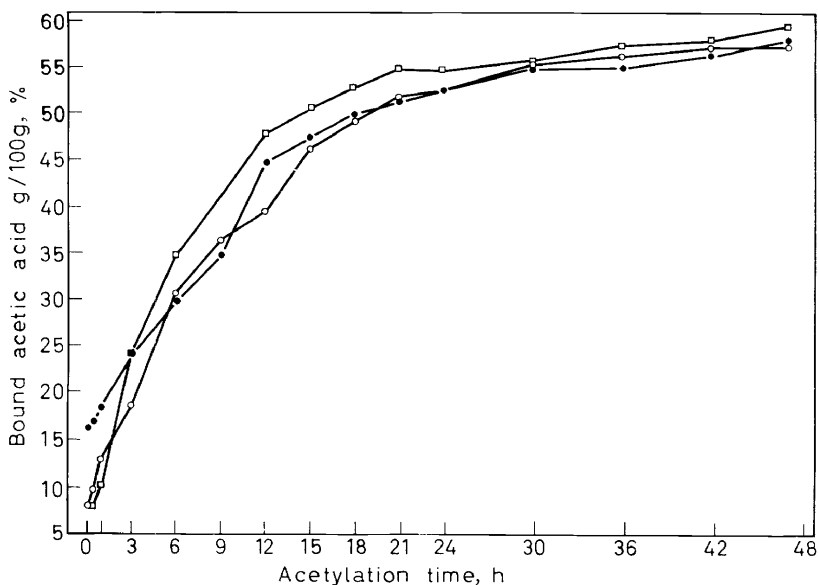

Figure 3. The amount of bound acetic acid present at different acetylation time. The acetylations were carried out at [●, 0°C; ○, 5°C; □, 10°C]

Experiment B

In this experiment the acetylation mixture (same as under Experiment A) as well as the temperature (0°C) were constant whereas the amount of catalyst was varied: the catalyst amounted to 1·5, 2·25, 3·0 and 4·5 per cent of sulphuric acid. The results with 2·25 per cent and 3·0 per cent are intermediate values so that only the results with 1·5 per cent and 4·5 per cent of sulphuric acid are presented in *Figure 4*.

The inferences that can be drawn from these results are: (a) Here too, the parallelism between the curves for the two indicators is evident; (b) at 0°C, the amount of passive catalyst remains practically constant; (c) the higher the concentration in sulphuric acid, the sooner partial evolving of catalyst takes place.

When the esterification is pursued at 0°C for 48 h at different concentrations in catalyst, the curves representing the different amounts of combined acetic acid have practically the same shape as is illustrated in *Figure 5*.

It should be noted here that the values in *Figure 5* are given for an acetylation continued for 48 h, which does not mean that the end point of acetylation is reached. This does not apply to the amount of combined sulphuric acid.

In view of a possible heterogeneity in the distribution of the sulphuric acid some results are listed in *Table 1* instead of being presented by curves.

Table 1. Effect of catalyst (H_2SO_4) concentration on esterification after 48 h

Sulphuric acid involved (ml %)	(g/litre)	Average SO_4 in mixed ester	Combined acetic acid after 48 h†	$N_s + N_a$ after 48 h
1·50	2·684	4·066	57·45	2·888
2·25	4·026	5·11	57·10	2·907
3·00	5·368	6·48	55·30	2·988
4·50	8·052	7·98	52·50	2·901

† This is not the end point of the acetylation.

According to our experience one might conclude that at a definite concentration of combined sulphuric acid, which must still be determined, the expulsion of the catalyst by the fibres occurs at an approximate value of 45–48 per cent of combined acetic acid.
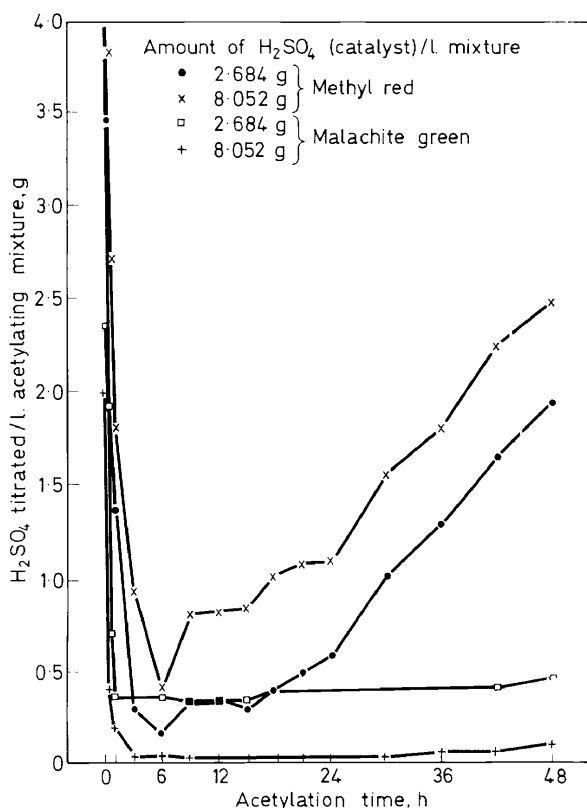
Figure 4. The effect of catalyst (H_2SO_4) concentration on acetylation at constant temperature

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Experiment C

In this experiment the temperature (°C), the amount of non-solvent and the content of sulphuric acid (1·5 per cent) were kept constant whereas the amount of acetic acid was varied and gradually replaced by acetic anhydride. The experiment was carried out with the acetylation mixtures given in *Table 2*.
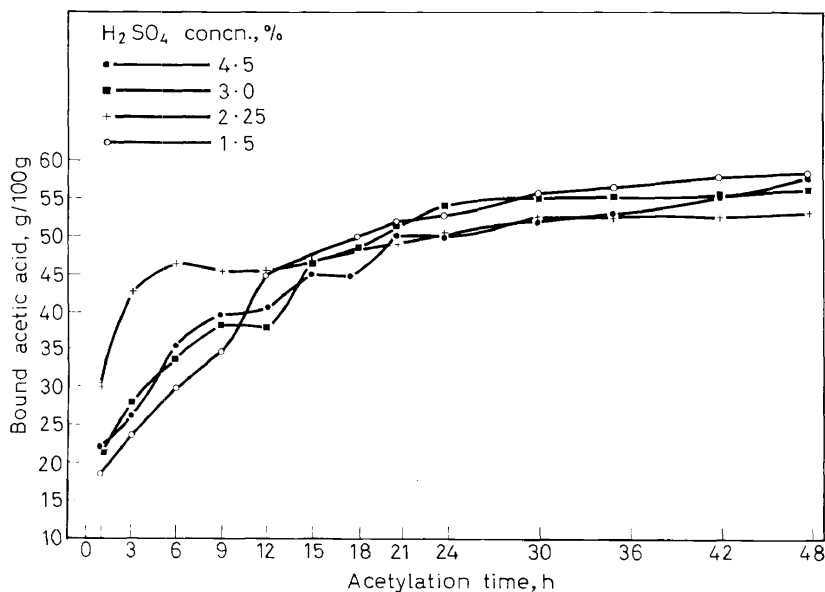

Figure 5. Effect of H₂SO₄ (catalyst) concentration on esterification at 0°C when the esterification is carried out for 48 h

Table 2. Composition of acetylating mixtures used in experiment *C*

Non-solvent (% by vol.)	Acetic anhydride (% by vol.)	Acetic acid (% by vol.)
60	20	20
60	25	15
60	30	10
60	35	5

From the results obtained it should suffice to mention that the substitution of acetic anhydride for acetic acid, the total amount of both remaining the same, does not exert a marked influence on the amount of free sulphuric acid in the liquid. At 0°C this amount always remains limited after the celluloses have been added. Likewise, the substitution of acetic anhydride for acetic acid does not affect considerably the amount of combined acetic acid. This, however, does not apply to very low concentrations of the anhydride in the acetylating mixture.

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Experiment D

In this final experiment the influence of the nature of the non-solvent was examined and here the temperature (0°C) and the concentration of sulphuric acid (1·5 per cent) were kept constant whereas the nature of the non-solvent was varied: benzene, toluene and xylene. The results of the different determinations of sulphuric acid are given in *Figure 6*.
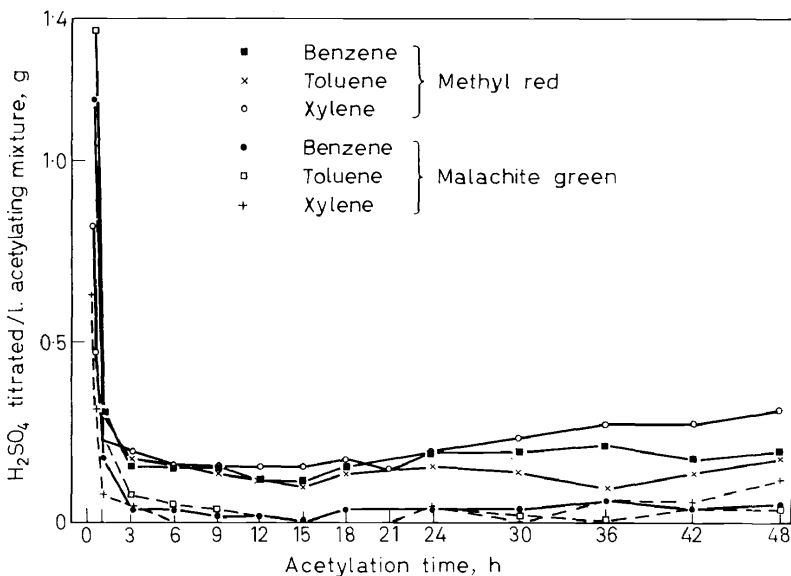

Figure 6. Effect of the non-solvent (benzene, toluene, and xylene) on esterification carried out in the presence of cellulose at 0°C; catalyst (H_2SO_4) concn. 1·5 per cent

These results show beyond doubt the prominent part played by the celluloses in the migration of the sulphuric acid during the acetylation, independently of the more or less easy sulphonation of the hydrocarbons used as non-solvent. In order to prove this it is sufficient to compare the last mentioned *Figure 6* with the curves showing the evolution of the sulphuric acid in the absence of cellulose.

The curves of the combined acetic acid and the combined sulphuric acid have the same outlook at 0°C. Since the differences between the determined values are slight and fall within the range of the measurement they have not been given.

Influence of the mechanical form of the celluloses

Another advantage of the heterogeneous acetylation is that according to this method it is possible to examine the influence of the mechanical form the celluloses have, just prior to the esterification, on the chemical and other properties thereof. This study can be pursued in particularly advantageous conditions, when the static esterification is applied, i.e. in the absence of mechanical stirring during the acetylation.

In order to examine this influence the following procedure is adopted. At different intervals of the acetylation samples are taken, washed, stabilized,

rinsed till neutral and dried. The viscosity of a solution in methylene chloride–alcohol (expressed in centipoise or dyne-seconds), the solubility, the content of combined acetic acid and the filterability are then determined. By filterability is understood the amount of solution of triacetate, in a specific amount of solvent, that can be filtered under a specific pressure through a specific surface of a specific quality of filter medium. The complete clogging of the filter determines the end of the test.

In order to determine the influence of a given treatment one examines the comparative curves.

Determination of the mechanical form of celluloses

The mechanical form of the celluloses is determined by the following factors.

1. The nature of the celluloses themselves, e.g. mill-run, first-cut and second-cut in the case of the bleached linters, and hardwood or resinous in the case of the wood pulp.

2. The nature and intensity of some treatments: physical, mechanical as well as chemical treatments that the celluloses have undergone on the site where they are produced, such as heating, jordaning, carding, drying, etc.

3. The nature and intensity of some physical, mechanical and chemical treatments that the celluloses have undergone in the establishment where they are esterified such as in the case of linters the nature of opening, in the case of wood pulp the nature of the shredding, the temperature at which the water content of the cellulose was reduced, etc.

Factors that *adversely* affect the mechanical form are:

(a) Abnormal disparity in the fibre length. Fibres that are too short as well as dust favour the formation of less penetrable agglomerates. Fibres that are too long, when dipped into a liquid, usually stick together in a strand-like form which reduces to a large extent the permeability of the agglomerate. This is illustrated by a piece of wound cotton which, when dipped into a liquid, intertwines to form less penetrable agglomerates.

(b) Insufficient or excessive opening in the case of linters and shredding in the case of wood pulp. Hard pressed linters or unshredded pieces of sheet are, of course, less penetrable whereas excessive opening or shredding, when not followed by an additional appropriate mechanical treatment, gives rise to what occurs in the case of fibres that are too long.

(c) An anomaly in the drying process, e.g. a far too important water content of the celluloses to be dried, too prolonged a drying time, and an excessive drying temperature for the celluloses, or a combination of these three factors can damage, even permanently, the celluloses. These factors can result in a kind of felting, a local chemical modification, or an increase in the percentage of the crystalline fraction.

In *Figures 7* and *8* a comparative examination is given of the viscosity and the filterability of the same linters, which have been acetylated a first time after normal reduction of the water content and a second time after a remoistening with their weight in water, followed by a redrying at 125°C. The acetylations occurred under exactly similar conditions. The difference

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between both products is remarkable. It should be noted that the real difference in filterability is still larger than represented. At equal concentrations in the solutions of a triacetate with equal solubility, a lower viscous triacetate will give indeed a higher filterability. In this case the viscosity of the non-dried cellulose is markedly higher.
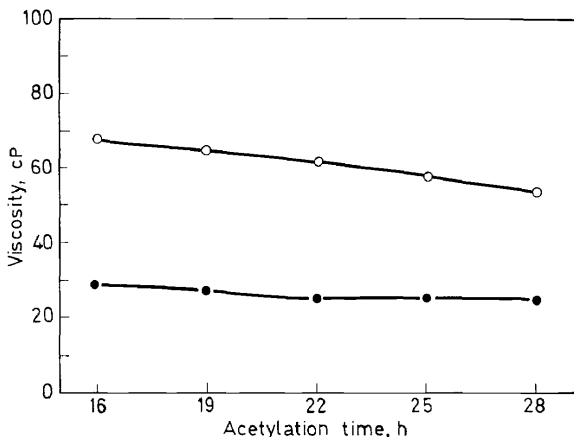

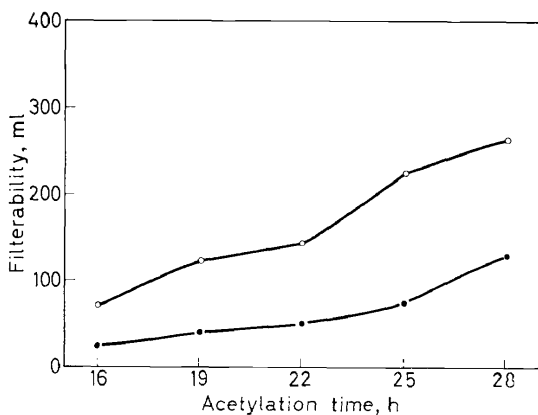*Figure 7.* Effect of acetylation time on viscosity of linters [○, standard, not dried; ●, humidified to 100 per cent and dried at 125°C]

Figure 8. Effect of acetylation time on the filterability of linters [○, standard, not dried; ●, humidified to 100 per cent and dried at 125°C]

Factors that *favourably* influence the mechanical form are:

(a) A swelling of the fibres and keeping them swollen just before they are pretreated. The advantage of this treatment is shown by the following test. A cellulose is normally pretreated. Another sample of the same cellulose is remoistened with water. After 1 h the excess of water is washed out by means of acetic acid.

Both celluloses were acetylated under the same conditions and the results of the comparative examination are given in *Figures 9* and *10.*
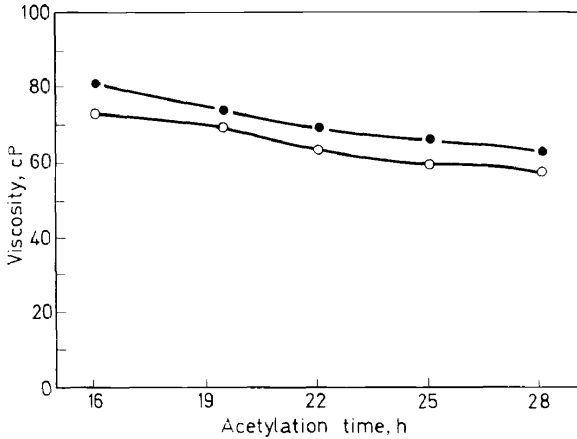
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Figure 9. Effect of acetylation time on viscosity in the case of *pretreated* cellulose [○, standard, not humidified, not dried; ●, humidified completely, washed twice with acetic acid, not dried]
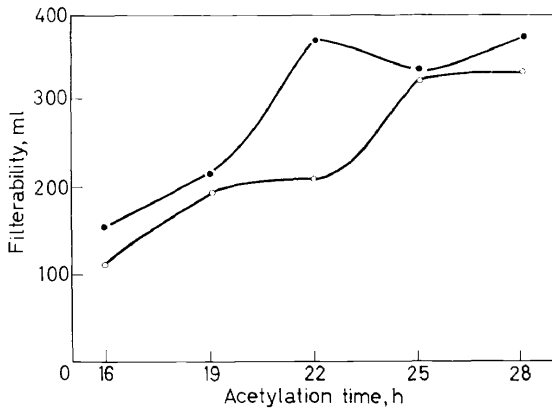

Figure 10. Effect of acetylation time on filterability in the case of *pretreated* cellulose [○, standard, not humidified, not dried; ●, humidified completely, washed twice with acetic acid, not dried]

Notwithstanding its higher viscosity, the acetate produced with the pre-swollen fibres shows a higher filterability.

(b) The mechanical treatment that the fibres undergo during the pretreat-ment. An adequate mechanical treatment results in

1. A modification of the fibre itself. The microscopic examination of fibres thus treated shows the following (a) Fissures mainly oriented parallel to the fibrils. Some clefts may also run transversely to the axes of the fibrils (*Figure 11*). (b) Fibrillation: Some of the wall layers may be separated from the fibres and appear as a loose material in the form of fibrillar bundles, ribbon shaped bundles or thin membraneous fragments (*Figure 12*). (c) Occasionally: Ruptured fibres (*Figure 13*).

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2. A modification in the aggregation of fibres. This treatment aims at the formation of spherical aggregates called "pills", which prevent that by some kind of felting, larger, less penetrable agglomerates of fibres form. The "pills" themselves show an excellent penetrability. As a result thereof the liquid reagents can very easily reach the interior of the agglomerate, flow through it and leave it.
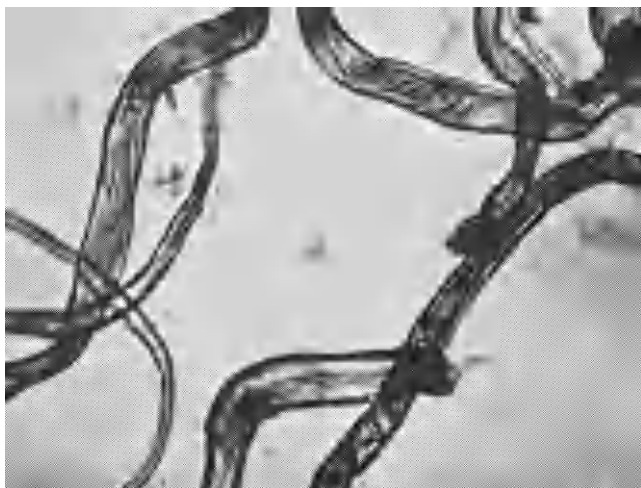

Figure 11. Microscopic examination of the fibre showing fissures mainly oriented parallel to the fibrils. Some clefts also run transversely to the axes of the fibrils

Figure 12. Microscopic examination of the fibre showing fibrillation

3. An additional opening of, by accident, insufficiently opened or shredded aggregates which may occur locally, or of locally felted cellulose.

The advantages of the mechanical pretreatment are:

1. A decrease or even a total elimination of the "ageing" which means that in most cases the celluloses may be esterified immediately after this pretreatment without any risk as to the quality of the end-product.

2. As a result of the easier penetration of the reagents not only nto the agglomerates of fibres but also in the fibres themselves it can be stated that this mechanical treatment does indeed shorten the reaction time.

Figure 13. Microscopic examination of the fibre showing ruptured fibres
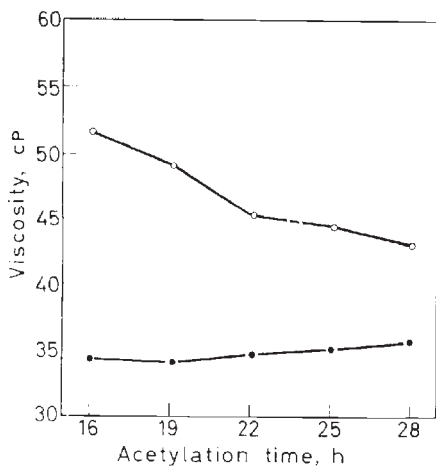

Figure 14. Effect of acetylating time on viscosity under: ○, mechanical pretreatment; ●, statical pretreatment

3. A higher viscosity of the end-product, most probably resulting from an increase in the reactivity. This increase clearly appears from a comparison of the viscosity curves of the same celluloses acetylated in the same conditions but once without and once with mechanical pretreatment.

Figure 14 also shows very clearly the favourable influence of the mechanical pretreatment.

4. A higher filterability most probably resulting from a higher degree in homogeneity of the triacetate that has been pretreated mechanically. For it is to be expected that a higher homogeneity can be reached when the liquid reagents can easily come into contact with every part of the fibre. *Figure 15* shows how the quality of the end-product is advantageously influenced by this mechanical pretreatment.
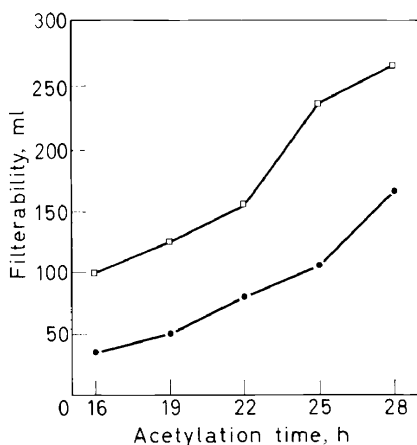

Figure 15. Effect of acetylating time on filterability under: ○, mechanical pretreatment; ●, statical pretreatment