

UNITED STATES PATENT OFFICE

2,559,914

PROCESS FOR THE PRODUCTION OF
CELLULOSE SULFURIC ACID ESTERS

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No Drawing. Application December 13, 1946, Se-
rial No. 716,176. In Belgium December 5, 1942

6 Claims. (Cl. 260—215)

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The cellulose sulphuric esters have up to now, in contrast to other water or alkali soluble cellulose derivatives, not found the recognition due to them on account of the easy accessibility of their starting materials and of their suitability as adhesive, wetting and thickening materials. This is mainly due to the fact that the methods hitherto known for their production have been either too troublesome and uneconomical or that the products were largely decomposed.

A method has now been devised which resembles the well known method for nitration of cellulose, in which the esterification of the cellulose is carried out in an esterification bath containing sulphuric acid, the fibrous structure being maintained. This offers not only the advantage that after the esterification the bath could be separated and used again but also that considerable decomposition of the cellulose can be avoided, a fact common to all processes in which the cellulose enters into solution when esterified in an acidic bath. From a technical point of view, the new process is also distinguished from the usual ones in that it does not use sulphuric acid anhydride or sulphuryl chloride or other chloro-sulphonating agents which split off hydrochloric acid, but simply sulphuric acid itself; furthermore it is not necessary to cool strongly during the esterification. In comparison with these processes for the production of sulphuric acid esters which have as starting material the alkali celluloses, the new process also possesses the advantage that wood may be used as a starting material, the bond between cellulose and lignin being broken by the sulphuric acid.

The new process uses dry cellulose in the form of linters, pulp or wood (in the last two cases after having been sufficiently divided in order to procure a sufficiently large surface area, e. g. in the form of paper, flock of pulp, wood-flour or sawdust) which is introduced into a cooled bath of sulphuric acid and an alcohol, the ratio of sulphuric acid to alcohol being so chosen that on the one hand the dissolution of the cellulose is prevented and on the other a partial esterification of the cellulose is achieved.

As to the alcohols in the esterification bath, the lower aliphatic alcohols are used, e. g. methyl, ethyl, propyl, butyl, amyl and hexyl alcohols, and those higher alcohols which are perfectly miscible with sulphuric acid, excepting the isomers labile in sulphuric acid. Cyclic alcohols such as cyclohexanol, can be used just as substituted alcohols as the glycolethers, for example, monobutylglycol. Mixtures of several alcohols are of course also ap-

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plicable and the use of an unsaturated aliphatic alcohol is not precluded.

As already mentioned the proportion of the alcohol in the esterification bath is such that on the one hand the cellulose in the esterification bath retains its fibrous structure until the end of the esterification reaction and on the other hand that the degree of esterification and the esterification velocity of the cellulose is controlled in the desired manner. The sulphuric acid distributes itself between the OH groups of the cellulose and those of the alcohol and the sulphuric acid ester of the alcohol acts at the same time catalytically, by exchange of radicles. The proportion of alcohol in the esterification bath which still permits the cellulose to retain its fibre structure, is of course different with different alcohols; it changes with the molecular weight of the alcohol and its structure and has to be obtained by preliminary investigation. In general, there is the following rule: an increasing molecular weight of the alcohol permits an increasing proportion of the alcohol in the esterification bath. From the illustrative examples it is clear that the alcohol sulphuric acid mixtures contain, with respect to the molecular proportion, a large excess of sulphuric acid over alcohol. The sulphuric acid esters of the alcohols are therefore partly formed in these mixtures and these are present at the same time as the uncombined alcohol and sulphuric acid. Thus, any other method, apart from the above mentioned can be used for the preparation of the esterification bath containing alcohol-sulphuric acid esters in an excess of sulphuric acid in such a proportion that the fibrous structure of the cellulose is maintained. These esters could be made in any other way and introduced into excess sulphuric acid. As however the preparation of the esterification bath by mixing alcohols with excess sulphuric acid is the simplest way, it is mainly this method which will be described. It has been found that in general, mixtures containing the alcohol and the sulphuric acid in the proportions which are limited on the one hand by the molecular ratio 1:1 and on the other by the ratio 1:3 are capable of fulfilling the conditions required for esterifying the cellulose without its dissolution. When the limit 1:1 is approached, the mixture not containing an excess of sulphuric acid, the reaction becomes too slow, whereas when the limit 1:3 is approached, a large excess of sulphuric acid being now present, the fibres start to dissolve in the bath.

Apart from the alcohol-sulphuric acid esters

(or alcohols and sulphuric acid) other substances can be present in the esterification bath, e. g., other acids or aromatic compounds such as benzene and others.

Starting from pure cellulose, the completion of the esterification can be recognised by the fact that a sample withdrawn from the bath dissolves completely in water; depending upon the conditions chosen, a few minutes to several hours are necessary for this.

After completion of esterification, the fibrous mass, which has swollen up considerably, is separated from the esterification bath by centrifuging or by filtering off, after which the acid sulphuric acid esters of cellulose (or monoester of the sulphuric acid) may be isolated in various ways. Thus, the cellulose ester can be freed from most of the residual acid by washing with methyl or ethyl alcohol or any other alcohol, which could be the same as the one with which the esterification was carried out. Finally, the stable salt of the cellulose sulphuric acid ester is obtained by neutralization.

The alcohol in the esterification bath can be regained by the addition of water and distillation; alternatively, the esterification mixture obtained after separation of the fibrous mass can be adjusted in composition and then used for treatment of a new quantity of cellulose; or it may be worked up to an ester after the addition of a fatty acid; or finally converted by neutralization to the salt of a sulphuric acid ester, which can be used itself as a wetting agent.

During the washing process following esterification, which may be carried out not only with alcohols but also with esters or ethers, such as ethyl acetate or ethyl ether, and especially when lower alcohols are used as washing agents, there sometimes takes place a partial dissolution of the cellulose ester. After partial saponification of the cellulose ester a reprecipitation of a lower cellulose ester soon occurs.

As to the washing of the sulphuric esters of cellulose with an alcohol, an ester or an ether, it can be carried out several times as demonstrated by the examples.

It is also possible to use for this purpose successively different combinations. A final wash with methyl alcohol gives products a superior stability, up to 180° C.

Should it be considered desirable to preserve the fibre structure from beginning to end of the preparation of the cellulose sulphuric acid ester salts, neutralization of the acidic cellulose esters, washed if necessary, is carried out with an alcoholic or aqueous alcoholic alkali solution, where the cellulose ester does not dissolve.

It only remains to wash and dry the product. In washing the ester, appropriate use may be made of the fact that the potassium sulphuric acid ester of cellulose is not soluble in cold 50% aqueous methyl alcohol. In the neutralization besides the alkalis, there may be used ammonia and amines.

If it is desired to separate the products obtained from the sulphonation of wood, after subsequent washing, that is, the cellulose sulphuric acid esters from lignin it is unnecessary to avoid a dissolution of the cellulose sulphuric acid esters, before, during or after the neutralization. After dissolution of the ester the remaining lignin is then centrifuged or filtered off and the alkali salt of the sulphuric acid ester may be precipitated from the solution with alcohol.

A modification of the above entails completely

the washing of the obtained fibrous cellulose sulphuric acid ester and neutralizing after separation from the ester bath directly by dissolution in an aqueous alkali solution. The solution obtained can be freed from admixed salt in various manners, for instance by precipitation or dialysis and then from here the cellulose esters can be obtained by precipitation with alcohol or by vaporation in a vacuum.

The products obtained according to one of the above described methods are the salts of cellulose sulphuric acid esters with a low sulphuric acid content which corresponds roughly to that of the monoester of the cellulose. Its molecular weight is high.

There is the possibility that in treatment of the cellulose with the above described baths there is also some combination of the alcohols with cellulose to form glucosides; it was not, however, possible to confirm this with the small quantity of alcohol in question here.

The products obtained in the present process are stable to 160° and not hygroscopic. On soaking they give a clear aqueous solution of high viscosity which strongly resembles glycerin. Dilute solutions do not decompose at 100°, and concentrated solutions give on cooling solid gelatinous masses which are liquefied by heating again.

Cellulose sulphuric acid esters of this kind, having a very high molecular weight, have not previously been described. They are a new product with remarkable properties which may find application for very diverse uses, e. g. as glues, dressings, starch substitutes, wetting agents, emulsifiers, washing agents, thickening agents, coatings, intermediate layers for safety glass, protective colloids, impregnating materials and the like. They are generally applicable in the textile industry and form, if necessary after the addition of a foaming agent, an excellent soap substitute.

It has been found that the starting material for the preparation of these sulphuric esters is not limited to cellulose, and that other materials containing polysaccharides as e. g. starch are also suitable for this purpose; in these cases, one proceeds in a quite analogous manner.

With regard to the uses of these new products, the following can still be mentioned: since a thin film of this cellulose sulphate adheres particularly well to a film of another cellulose derivative, these products can be employed as an intermediate layer for fixing gelatine to nitrocellulose or to cellulose acetate, or as antistatic layer for moulded articles of these derivatives, due to the ionised condition of the sulphate. It can equally serve as a non-inflammable varnish. Contrary to the glycolates of cellulose which precipitate in moderately strong acid, the sulphates of cellulose described above are not excluded from use under these conditions. They are also capable of being employed as starting materials for therapeutics, serving to prevent the coagulation of blood; P. Karrer has summarized the use of cellulose sulphate for this purpose (*Helv. Chim. Acta*, 26, 1296). The fact that cellulose can be extracted directly from wood by means of the above procedure, allows of the possibility of its use in the field of the saccharification of wood and for the determination of the lignin in the wood.

Examples

1. 13 parts by weight of primary n-butyl alcohol and 74 parts of sulphuric acid, representing

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a molecular proportion of alcohol to acid of 1:4.3, are mixed with cooling. When 10 parts of dried linters are introduced into the mixture, maintained at 20° C., they swell very strongly after only a few minutes and start to dissolve in the bath, so that it is no longer possible to separate them.

2. Keeping the temperature at 20° C., 10 parts of dried linters are introduced progressively into a mixture made by adding, with cooling, 110 parts of sulphuric acid to 29 parts of primary n-butyl alcohol, which represents a molecular proportion of butyl alcohol to sulphuric acid of 1:2.8. After ten minutes the fibres, which are on the point of forming a paste, are separated, washed twice with diethyl ether and neutralized with a solution of potash in methyl alcohol containing 20% of water and washed with methyl alcohol containing 50% of water. The sulphuric ester of cellulose thus obtained, gives a viscous solution in water, free from fibres.

3. Into a mixture composed of 32 parts of butyl alcohol and 103 parts of sulphuric acid, which represents a molecular proportion of butyl alcohol to sulphuric acid of 1:2.5, 10 parts of dried linters are introduced, keeping the temperature at 25°. After 45 minutes, the product is separated, washed three times with methyl alcohol and then treated in the manner described in the preceding example. This gives a sulphuric ester of cellulose which dissolves in water with a high viscosity.

4. The mixtures containing butyl alcohol and sulphuric acid in the ratios of 1:2.1 and 1:1.5 give the same good results as in Examples 2 and 3, providing that the duration of the reaction is increased to 1 hour and a half and to 12 hours respectively; whereas a mixture containing the two components in equimolecular proportions 1:1 no longer esterifies the cellulose, even after a long period.

The other alcohols behave in a manner analogously to butyl alcohol, and it is not necessary to give examples.

I claim:

1. A process for the production of fibrous cellulose sulfate which comprises reacting cellulose

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with a mixture containing an aliphatic sulfate and sulphuric acid, there being present in said mixture from about one to about three moles of sulfate radical per mole of aliphatic radical, said aliphatic sulfate being derived from a sulphuric acid miscible aliphatic alcohol excepting isomers thereof labile in sulphuric acid.

2. A process for the production of fibrous cellulose sulfates which comprises reacting cellulose with a mixture consisting essentially of an aliphatic sulfate and sulphuric acid, said mixture comprising the esterification reaction mixture of sulphuric acid with an aliphatic alcohol miscible with sulphuric acid excepting isomers thereof labile in sulphuric acid, there being employed from one to about three moles of said sulphuric acid per mole of said alcohol in said esterification reaction.

3. The process of claim 2 wherein the aliphatic alcohol employed in the formation of the aliphatic sulfate is selected from the group consisting of methyl, ethyl, propyl, isopropyl, butyl, amyl, isoamyl, hexyl, and cyclohexyl alcohol and monobutyl glycol.

4. The process of claim 2 wherein cellulose in the form of linters is employed as a starting material.

5. The process of claim 2 wherein cellulose in the form of comminuted wood is employed as a starting material.

6. The process of claim 2 wherein the aliphatic sulfate is butyl sulfate.

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