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PRODUCTION OF CELLULOSE

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This invention relates to the production of cellulose from naturally occurring materials containing it.

It has been proposed to obtain cellulose from ligno-cellulosic material, in particular wood, by heating the material with a concentrated aqueous solution of chloracetic acid; a large proportion of the non-cellulosic constituents of the material goes into solution in the aqueous chloracetic acid, and a fairly pure form of cellulose can be separated by filtration and washing.

This process however has certain disadvantages. For one thing, a serious amount of corrosion of the reaction vessel may occur; for another, it is difficult to produce successive batches of cellulose having substantially the same properties, even from the same stock of wood, when using recovered chloracetic acid; for another, the amount of chloracetic acid recoverable is unduly low, especially having regard to the high cost of this reagent. It is an object of the present invention to overcome these disadvantages.

We have found that a major factor giving rise to each of these disadvantages is hydrolysis of the chloracetic acid, resulting in the liberation of free hydrochloric acid. We have also found that the amount of such hydrolysis occurring can be very greatly reduced, or even rendered negligible, and a good yield of cellulose of a satisfactory degree of purity can still be obtained, if the chloracetic acid is dissolved in or diluted with a substantially anhydrous organic substance which does not react with it at the treatment temperature and which, at least at the treatment temperature, forms with the chloracetic acid a single liquid phase. If desired the chloracetic acid can be replaced by another chlorinated lower fatty acid, but generally speaking chloracetic acid is the most convenient and cheapest chlorinated lower fatty acid to use, and its use is preferred. The term "lower fatty acid" is employed to denote fatty acids containing not more than 4 carbon atoms.

According to the invention therefore cellulose is produced from ligno-cellulosic material by a process which comprises heating the material with a substantially anhydrous homogeneous liquid mixture of a chlorinated lower fatty acid, preferably chloracetic acid, and an organic substance which does not react with it.

The ligno-cellulosic material may be employed in the ordinary air-dry state, and the expression "substantially anhydrous mixture" as applied to the treating mixture includes mixtures containing such relatively small mounts of water as

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might be derived from the ligno-cellulosic material.

The organic substance with which the chlorinated fatty acid is mixed may be regarded as either diluting or dissolving it (since most of the chlorinated fatty acids are solids at ordinary temperatures, though molten at the treatment temperatures) but for the sake of convenience it will be referred to in the present specification as a diluent; for the same reason the invention will be described in more detail by reference to the treatment of wood with chloracetic acid, though it will be understood that the chloracetic acid can if desired be wholly or partly replaced by another chlorinated lower fatty acid, e. g. dichloracetic acid, trichloracetic acid, or one of the mono- or di-chloropropionic acids, and that ligno-cellulosic materials other than wood can also be treated.

The diluent may be a low-boiling liquid such for instance as ethyl acetate, acetone or chloroform, and as the treatment temperature will usually be above the normal boiling point of such a compound it will then be necessary to carry out the treatment under pressure. We prefer, however, to use much higher boiling compounds, in particular compounds of normal boiling point above about 110° C. and advantageously between about 115° and 150° C. for instance hydrocarbons and hydrocarbon mixtures boiling within these limits, especially aromatic hydrocarbons containing 8 carbon atoms, normally liquid nitro- and halogenated aromatic hydrocarbons, lower fatty acids containing 2–4 carbon atoms, and fatty acid esters boiling at temperatures above 110° C. Examples of individual compounds which give very satisfactory results are xylene (including o-, m-, and p-xylene and mixtures of two or more of these isomers), ethyl-benzene, nitrobenzene monochlorobenzene, acetic acid, propionic acid, ethyl valerate or isovalerate and ethyl chloracetate, and of these we prefer to use the specified aromatic hydrocarbons, lower fatty acids, or fatty acid or chlorinated fatty acid esters.

Generally the chloracetic acid and the diluent will form a single liquid phase at all temperatures between room temperature (say about 15° C.) and the treatment temperature.

The relative proportions of the chloracetic acid and the diluent in the mixture may vary over a considerable range, but it is preferred to employ mixtures containing between 45% and 85% by weight of chloracetic acid; with the more resistant woods, e. g. spruce, the mixture may with advantage contain about 65%–80% of chloracetic

acid, while with easily attacked woods, e. g. poplar, chloracetic acid contents down to 50% are very suitable. Advantageously, the wood may be treated with at least 3 times, and preferably 5 or more times, its weight of the mixture at a temperature which is preferably above 120° C. and especially between about 130° C. and 140° or 150° C.

It is advantageous to employ as diluent a compound such that the mixture boils within or near the range 125° C. to 140° or 150° C., especially acetic acid, xylene or ethyl benzene, or ethyl chloracetate, and to carry out the process by boiling the mixture under reflux conditions. Other methods, e. g. heating under constant volume conditions, may however be adopted if desired. At temperatures of about 130°–140° C. the treatment usually requires about 1–5 hours, depending in part on the nature of the wood being treated.

When the wood has been treated with the mixture of chloracetic acid and diluent for the required time, the resulting cellulose may be filtered off as completely as possible and then washed, preferably with further quantities of the diluent or with acetone. Thus, when a mixture of chloracetic acid and glacial acetic acid or xylene has been employed, the cellulose may be washed with further quantities of hot or cold glacial acetic acid or xylene (as the case may be) until little or substantially no chloracetic acid remains on the cellulose, after which the cellulose may be washed free from acid with water or from xylene with a volatile organic solvent, e. g. acetone, alcohol, isopropyl ether or a low boiling hydrocarbon fraction consisting of hexanes with or without lower hydrocarbons. On the other hand, especially, but not only, when xylene or an ester has been used as the diluent, the cellulose may be washed free from chloracetic acid with acetone, after which it may if desired be freed from acetone by heating it in a current of air.

After being washed, the cellulose may be heated for a short time with an alkaline solution, preferably a caustic alkali solution of concentration between 0.25% and 2%, to decompose any cellulose chloracetate that may have been formed, and may then, if desired, be given a bleach, e. g. with hypochlorite or sodium chlorite, and/or any other desired purification treatment, for example a treatment with alkali. In particular the bleached or unbleached cellulose, which is already of a fairly high degree of purity, may be treated with a warm caustic soda solution of concentration between 15% and 22%, as described in our co-pending United States applications Ser. No. 75,963, filed 11th February, 1949, now Patent No. 2,645,576, and Ser. No. 154,886, filed April 8, 1950, now Patent No. 2,645,577, or the unbleached cellulose may be given one of the other purification treatments referred to in United States application Ser. No. 75,963.

In order to recover the chloracetic acid and diluent, the filtrate obtained after the main treatment, preferably together with the first wash liquors, may be diluted with a fairly high proportion of alcohol or water, preferably at room temperature or below, so as to precipitate the lignin, which may then be filtered off or otherwise separated. The alcoholic or aqueous acid remaining may then be reconcentrated, preferably by a solvent extraction method carried out in the cold; for example aqueous chloracetic and acetic acids may be concentrated by extraction with mixtures of ethyl acetate and benzene. In an alternative method the chloracetic acid and diluent (and the washing agent if the cellulose has been washed with a liquid other than the diluent, e. g. acetone) may be distilled directly from the filtrate, leaving the ligning as residue. The later wash liquors contain little or no chloracetic acid or lignin, and may be treated to recover the diluent in any desired way. The chloracetic acid and the diluent recovered may be employed in the treatment of further quantities of wood, the concentration of the chloracetic acid in the mixture being adjusted as may be desired or necessary.

While the new process is applicable to various types of ligno-cellulosic material, including cereal straws and the residues of other annual plants, it is particularly useful and its advantages are most apparent in the treatment of woods, including both coniferous and deciduous woods, for example, spruce, larch, fir, poplar and beech. It is found that the yields of cellulose obtained are very considerably greater, e. g., between about 13% and 20% greater depending on the type of wood treated, than those obtained when pulping by a conventional alkali type process such as the soda or sulphate process, following a dilute acid pre-hydrolysis; moreover, the quality of the cellulose obtained, as determined by its alpha-cellulose and pentosan contents and also by the clarity and viscosity of cellulose acetate made therefrom, is in many cases also higher.

The invention is illustrated by the following examples:

Example 1

Spruce chips were added to 6 times their weight of a mixture of 75 parts by weight of chloracetic acid and 25 parts by weight of glacial acetic acid, and the mixture boiled under reflux for 1½ hours. The acid mixture was then separated from the cellulose by filtration as thoroughly as possible, and the cellulose washed first with acetic acid and then with water until it was free from acid; the acetic acid washings were added to the original filtrate, the water washings being kept separate. The cellulose was then bleached in two stages with hypochlorite, washed and further treated with alkali to reduce its pentosan content. The purified cellulose had an alpha-cellulose content of 98% and a pentosan content of 1.29%; on acetylation it gave a cellulose acetate of viscosity 30 and clarity 41; the corresponding figures for cellulose made from the same wood by a soda pulping following an acid prehydrolysis and purified in the same way were: alpha-cellulose content 93.2%, pentosan content 1.38%, cellulose acetate viscosity 18, cellulose acetate clarity 14. The yield of purified cellulose was 37.6% compared with 33.2% by the soda process following prehydrolysis. (The figures for viscosity and clarity are on an arbitrary scale and are given for purposes of comparison only.)

Example 2

Poplar chips were treated as described in Example 1, except that a 50:50 mixture of chloracetic and acetic acids was used, and the boiling was continued for 4 hours. The purified cellulose had an alpha-cellulose content of 98.2% and a pentosan content of 2.08%. The yield was 40.0% compared with 34.4% by the soda process following prehydrolysis.

Example 3

Beech chips were treated as described in Example 1, except that a 65:35 mixture of chloracetic and acetic acids was used, and the boiling was continued for 4 hours. The purified cellulose had an alpha-cellulose content of 97.0% and a pentosan content of 1.81%. The yield was 34.7% compared with 30.2% by the soda process following prehydrolysis.

Example 4

Eucalyptus chips were boiled under reflux for 3 hours with 5 times their weight of a mixture of equal parts by weight of chloracetic acid and xylene. The crude cellulose so obtained was separated by filtration from as much of the treating mixture as possible, and was then washed with acetone until free from chloracetic acid, xylene and separated lignin. (The washings, after removal of the acetone by distillation, were added to the remainder of the separated treating mixture for recovery and re-use of the chloracetic acid and xylene.) The washed cellulose was boiled at atmospheric pressure for 30 minutes with a 1% aqueous caustic soda solution and was then bleached in two stages with hypochlorite and given a treatment with alkali to remove pentosans. The yield of purified cellulose was 41.1%.

Example 5

The process of Example 4 was repeated, except that the xylene was replaced by ethyl chloracetate. The yield of crude cellulose (i. e., after the boil with 1% caustic soda solution but before bleaching) was 49.5%; a bleach with sodium chlorite reduced this to 46.4%. The bleached cellulose, which had not been given a special pentosan-removing alkali treatment, had an alpha-cellulose content of 89% and a pentosan content of 3.95%.

Example 6

Wheat-straw was boiled for 4 hours with 8 times its weight of a mixture of equal parts by weight of chloracetic and acetic acids. The resulting cellulose was separated and washed as described in Example 1, and was then bleached with hypochlorite and given an alkali treatment to reduce its pentosan content. The yield of unbleached cellulose was 35.0%; the yield of bleached and purified cellulose was 31.0%, its alpha-cellulose content being 96.0%, its pentosan content 3.36%, and its mineral content 0.69%. If the straw, before being boiled with the chloracetic acid and acetic acid, was boiled first for 3 hours with a 1% hydrochloric acid solution and then for 2 hours with a 1% caustic soda solution, the corresponding figures were: Yield (unbleached) 28.0%, (bleached and purified) 23.0%; analysis or purified cellulose: Alpha-cellulose 93.2%, pentosan 1.50%, mineral 0.40%.

Having described our invention, what we desire to secure by Letters Patent is:

1. Process for producing cellulose from ligno-cellulosic material, which comprises heating ligno-cellulosic material to a temperature between 120° and 150° C. with an anhydrous homogeneous liquid mixture of a chlorinated fatty acid containing up to three carbon atoms in the molecule and an organic diluent inert to the chlorinated fatty acid, the concentration of the chlorinated fatty acid in the mixture being 45–85% by weight.

2. Process for producing cellulose from ligno-cellulosic material, which comprises heating ligno-cellulosic material to a temperature between 120° and 150° C. with an anhydrous homogeneous liquid mixture of monochloracetic acid and an organic diluent inert to the monochloracetic acid, the concentration of the monochloracetic acid in the mixture being 45–85% by weight.

3. Process for producing cellulose from ligno-cellulosic material, which comprises heating ligno-cellulosic material to a temperature of 125°–140° C. with an anhydrous homogeneous mixture of a chlorinated fatty acid containing up to three carbon atoms in the molecule and at least one normally liquid saturated hydrocarbon of boiling point between 115° C. and 150° C., the concentration of the chlorinated fatty acid in the mixture being 45–85% by weight.

4. Process for producing cellulose from ligno-cellulosic material, which comprises heating ligno-cellulosic material to a temperature of 125°–140° C. with an anhydrous homogeneous mixture of a chlorinated fatty acid containing up to three carbon atoms in the molecule and at least one aromatic hydrocarbon having the empirical formula C_8H_{10}, the concentration of the chlorinated fatty acid in the mixture being 45–85% by weight.

5. Process for producing cellulose from ligno-cellulosic material, which comprises heating ligno-cellulosic material to a temperature of 125°–140° C. with an anhydrous homogeneous mixture of a chlorinated fatty acid containing up to three carton atoms in the molecule and a fatty acid containing 2–4 carbon atoms in the molecule, the concentration of the chlorinated fatty acid in the mixture being 45–85% by weight.

6. Process for producing cellulose from ligno-cellulosic material, which comprises heating ligno-cellulosic material to a temperature of 125°–140° C. with an anhydrous homogeneous mixture of a chlorinated fatty acid containing up to three carbon atoms in the molecule and acetic acid, the concentration of the chlorinated fatty acid in the mixture being 45–85% by weight.

7. Process for producing cellulose from ligno-cellulosic material, which comprises heating ligno-cellulosic material to a temperature of 125°–140° C. with an anhydrous homogeneous mixture of a chlorinated fatty acid containing up to three carbon atoms in the molecule and an ester boiling between 115° and 150° C. of an acid containing 2 to 5 carbon atoms, selected from the group which consists of fatty acids and their chlorine substitution products, the concentration of the chlorinated fatty acid in the mixture being 45–85% by weight.

8. Process for producing cellulose from ligno-cellulosic material, which comprises heating ligno-cellulosic material to a temperature of 125°–140° C. with an anhydrous homogeneous mixture of a chlorinated fatty acid containing up to three carbon atoms in the molecule and ethyl monochloracetate, the concentration of the chlorinated fatty acid in the mixture being 45–85% by weight.

9. Process according to claim 1, wherein the cellulose produced is washed substantially free from chlorinated fatty acid by means of further quantities of the diluent.

10. Process according to claim 1, wherein the cellulose produced is washed substantially free from chlorinated fatty acid by means of acetone.

11. Process according to claim 2, wherein the cellulose produced is heated with an alkaline

solution to saponify any cellulose chloracetate that may have been formed.

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