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PRODUCTION OF CELLULOSE

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This invention relates to the production of cellulose and its conversion into cellulose esters and ethers of good quality.

The main sources of cellulose for conversion into cellulose esters and ethers are cotton linters and pulps obtained from wood. Of these, cotton linters are normally the purer form of cellulose. However, even they require a certain degree of purification, the ordinary practice being to boil the linters under pressure with a dilute alkali solution, e. g. a caustic soda solution of concentration below 5% and usually about 3%, and then to bleach them. While cellulose acetate, for example, of good quality can by careful working be obtained from cotton which has been given this treatment, it is generally not ideal from the moulders' point of view, in that during moulding a certain amount of colour is nearly always developed, presumably as a result of the high temperatures to which the cellulose acetate is raised during the moulding operation. It is an object of the present invention to produce a cellulose which is capable of being converted into cellulose acetate and other cellulose derivatives which can be moulded with as little colour change as possible.

According to the invention, cotton is given a purification treatment which comprises the step of subjecting it to the action of an aqueous caustic alkali solution of concentration 15%–25%, preferably 15%–20%, at a temperature at which it becomes partially, but not completely, mercerized. We have found that as a result of such treatment, the cotton can be acetylated to give a product which on moulding develops considerably less colour than when the cotton has been treated in the conventional way. The treatment with the 15%–25% caustic alkali solution preferably precedes or follows a pressure boil with caustic alkali of concentration below about 5%, especially a boil with a 2%–5% caustic alkali solution at a temperature of 120°–180° C. It is advantageous also to bleach the cotton either before or after the treatment with the 15%–25% caustic alkali solution, for example with chlorine or with sodium or calcium hypochlorite in acid solution or, especially if a particularly high viscosity product is required, with sodium chlorite. Both the pressure boil and the bleach may be carried out in one or more operations.

It is, of course, well known that complete mercerisation of cellulose by means of an aqueous caustic alkali solution takes place only below a definite temperature, which depends on the concentration of the alkali solution. Above this temperature is a range within which partial mercerisation occurs. A graph relating temperature and caustic soda concentration to the degree of mercerisation (i. e. whether it is partial or complete) is given in "Cellulose and Cellulose Derivatives" by Emil Ott (New York 1943) on page 274. For a 15% caustic soda solution the temperature below which mercerisation is complete is about 27° C.; for 20% caustic soda it is about 40° C.; and for 25% caustic soda it is about 48° C. In the practice of the invention it is advantageous to treat the cotton at a temperature which is higher than the maximum at which complete mercerisation occurs by 5° C. or more; thus a 15% caustic soda solution is preferably used at a temperature of about 32° C. or higher, and a 20% solution at about 45° C. or higher. The temperature should not be so high that little or no mercerisation occurs, and it is preferred not to exceed a temperature which is about 25°–30° C. above the maximum at which complete mercerisation occurs; thus it is preferred to work at a temperature within a range varying from about 32°–50° C., preferably 35°–45° C., with a 15% caustic soda solution, to about 45°–65° C., preferably 45°–55° C. with a 20% solution, and about 53°–75° C., preferably 55°–65° C., with a 25% solution. Very good results are obtained by using a 16%–18% caustic soda solution at about 37°–45° C.

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The treatment may be carried out by immersing the cotton in the caustic alkali solution at the desired temperature, if desired with stirring, for a period for instance between about 15 minutes and 5 hours and especially for about 20–90 minutes. Other methods may however be employed; for example the alkali solution may be sprayed on the cotton, though it may then be less easy to obtain a thorough and uniform treatment. The alkali solution may contain a small proportion of a wetting agent, for instant Turkey red oil (as may also a dilute alkali solution used in a pressure boil as described above). If desired, oxygen may be excluded during the treatment so as to reduce to the minimum any degradation suffered by the cellulose; for example the cotton may be introduced into a closed vessel which is evacuated before the alkali solution is run in, or the treatment of the cotton with the alkali may be conducted in an atmosphere of nitrogen.

At the end of the desired treatment period, the alkali may be run off or otherwise removed from the cotton, which may then be washed substantially free from alkali and dried. For example it may be washed with water until the washings no longer react alkaline, or it may be given one or more washes with a dilute acetic or other acid

solution, preferably preceded and followed by washing with water. For the various washes mains water may be used, but it is generally advantageous to employ distilled water or water which has been demineralised by an ion-exchange process, especially in the later stages of the washing. Finally, if desired, the cellulose may be washed with an organic liquid, especially acetone, to remove water, or it may be completely or partly freed from water by some other method, e. g. by means of a current of warm air, preferably without raising its temperature above about 60° C.

Although it is usually sufficient to subject the cotton to a single treatment with the 15%–25% caustic alkali solution, it may, if in any particular case it appears desirable, be given two or even more such treatments, preferably with a total duration of 20 minutes or more, either under the same or under somewhat different conditions falling within the specified limits. Such treatments may be consecutive, or they may be separated in the order of operations by other treatments, e. g. the dilute alkali pressure boil or bleaching operation already referred to. In any case it is advisable to wash the cellulose thoroughly after each treatment, though it is not essential to remove all traces of alkali or of course to dry the cotton before it is subjected to a further stage of the purification.

Cotton treated in accordance with the invention may be used in the production of organic derivatives of cellulose, and especially for making cellulose esters and ethers which are to be moulded. For example it may be acetylated by known methods, preferably after a pretreatment with glacial acetic acid with or without a small proportion of an acetylation catalyst, e. g. sulphuric acid or perchloric acid. When acetylation is substantially complete, the product may be ripened to reduce the acetyl content and modify the solubility properties of the cellulose acetate as may be desired; advantageously the ripening may be performed at a high or fairly high temperature after neutralising part or all of the acetylation catalyst. If desired the acetylation solution may be filtered before or, preferably, after the ripening. The ripened cellulose acetate may be precipitated in known manner, as by stirring in dilute acetic acid, and then thoroughly washed. It will generally be advisable to give the precipitated and washed cellulose acetate a separate stabilising treatment, for example by warming it with very dilute sulphuric acid or boiling it under pressure with demineralised or distilled water, and also if desired with an aqueous alcohol.

Cotton treated by the new process is also very suitable for conversion into other cellulose esters, e. g. cellulose propionate, cellulose crotonate, cellulose butyrate, cellulose stearate and cellulose benzoate, and also into mixed esters as for example cellulose acetate propionate, cellulose acetate butyrate and cellulose acetate stearate. The cellulose esters may, if desired, be purified by fractionation or extraction methods, in order still further to reduce the tendency to colour formation. When the cotton is to be used in the production of cellulose ethers, e. g. ethyl cellulose, it is not as a rule necessary to wash out all traces of alkali, but it is very desirable to wash thoroughly enough to ensure that substantially all the impurities dissolved by the alkali are removed.

The invention is illustrated by the following example; the "parts" given are in all cases parts by weight.

Example

Cotton linters were given a boil at about 50 p. s. i. g. with a 3% caustic soda solution, washed thoroughly, bleached with calcium hypochlorite in acid solution, and again thoroughly washed. The bleached linters were immersed for 30 minutes in a 17% caustic soda solution at a temperature of 40° C.; the caustic soda solution was then run off and the linters washed several times with mains water and then once with a 0.1% acetic acid solution, again with mains water and then three times with demineralised water. Finally the linters were washed once with acetone and allowed to dry at room temperature.

100 parts of the purified linters were activated by treatment with 50 parts of acetic acid at room temperature for 2 hours, and then cooled to 5° C. and introduced into about 600 parts of an acetylation mixture, cooled to 0° C., consisting of 40% of acetic anhydride and 60% of acetic acid and containing 12 parts of sulphuric acid. When acetylation was complete there was added a magnesium acetate solution of concentration and in amount such that all unchanged acetic anhydride was hydrolysed to acetic acid, 100 parts of additional water was added to the acetylation solution. and 11.5 parts of the sulphuric acid was neutralised. The solution was then ripened at a temperature of 90°–95° C. for about 2½ hours, after which the cellulose acetate was precipitated by stirring in dilute acetic acid. The precipitate was washed with mains water, and then stabilised by heating with distilled water for 1 hour to a pressure of 40 p. s. i. g. It was then washed to neutrality with distilled water and dried. The product had an acetyl value of 56.5%; on being moulded it developed considerably less colour than did cellulose acetate made in exactly the same way except that the treatment with the 17% caustic soda solution was omitted.

The process described above can be modified by subjecting the linters first to the treatment with the 17% caustic soda solution, then to the pressure boil and then to the hypochlorite bleach, care being taken to wash them very thoroughly affter the bleach, as well as after the other purification stages.

If desired about 1% (on the solution) of Turkey red oil can be employed in either or both of the alkali treatments.

While the invention has been particularly described by reference to processes in which the cotton is not only treated with the 15%–25% caustic alkali solution, but is also given a pressure boil with a dilute caustic alkali solution and a bleach, the treatment with the 15%–25% caustic alkali solution may be employed alone, or it may be supplemented by other purification steps. However, the processes described above represent the preferred method of putting the invention into practice.

In the claims, in order to distinguish clearly between the 15%–25% alkali solution and the dilute alkali solution used in a preceding or following pressure boil, the former will be referred to as a strong solution and the latter as a weak solution. It will be understood that the adjectives "strong" and "weak" do not import any limitations into the claims that are not already expressed in numerical terms.

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

1. In the purification of cotton linters by a

process which includes boiling the linters under pressure in a 2–5% caustic alkali solution and bleaching the linters, the improvement which consists in giving the linters a subsequent additional treatment with a caustic soda solution of concentration 15–20% at a temperature varying from 32–50° C. with a 15% solution to 45–65° C. with a 20% solution.

2. In the purification of cotton linters by a process which includes boiling the linters under pressure in a 2–5% caustic alkali solution and bleaching the linters, the improvement which consists in giving the linters a subsequent additional treatment with a caustic soda solution of concentration 15–20% at a temperature varying from 35–45° C. with a 15% solution to 45–55° C. with a 20% solution.

3. In the purification of cotton linters by a process which includes boiling the linters under pressure in a 2–5% caustic alkali solution and bleaching the linters, the improvement which consists in giving the linters a subsequent additional treatment with a caustic soda solution of concentration 16–18% at a temperature of 37–45° C.

4. Process according to claim 1, wherein at least one of the alkali solutions contains a wetting agent.

5. Process according to claim 1, wherein at the end of the purification treatment the linters are washed with aqueous washing liquors, at least the last stages of the washing being carried out with water substantially free from metal ions.

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