

UNITED STATES PATENT OFFICE

2,014,074

COMMINATION OF CELLULOSIC MATERIALS

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No Drawing. Application October 22, 1929,
Serial No. 401,619

11 Claims. (Cl. 260—101)

This application relates to processes for the comminution of cellulose and particularly to processes which render the cellulosic material more amenable to esterification.

Cellulosic materials have been comminuted in the past by either mechanical means in paper beaters and jordans or physico-chemically by dispersion in peptizing solutions, such as ammoniated cupric oxide, zinc chloride solution and the like. In the former case, intensive beating in water cannot comminute the cellulosic body without considerably hydrating it, so that resistance to further comminution is developed and the product does not effectively increase the subdivision beyond a certain point. In the case of solutions, the cellulose is, at the same time, considerably chemically degraded, and also is not readily separated from the solutions in finely divided form.

An object of the present invention is to provide a process whereby cellulosic materials may be rapidly comminuted. Another object of this invention is to provide a process for such comminution in which liquid dispersion mediums aid in the comminution. A further object of this invention is to provide a simultaneous pretreating and comminution process for the preparation of cellulose which fits it for acetylation. Other objects will hereinafter appear.

We have discovered that cellulosic materials may be comminuted to very fine dispersions and impalpable powders, and in a large degree to colloidal subdivisions, by mechanically grinding in the presence of excess of certain organic liquids. Not all organic liquids are suitable for the purpose. Apart from the instable substances, highly saturated bodies, and substances too easily autoxidized, we have discovered that a substantially definite criterion of applicability of organic liquids can be made in that we have found the most important factor to be the coefficient of friction given by the liquid in question as between the cellulose and the impelling surface. The coefficient of friction is

$$u = \frac{\text{friction}}{\text{load}}$$

There is a constant proportionality between the coefficient of friction u_a for a given fluid measured between two surfaces of the same material which will be designated as a , say, glass, and the coefficient of friction u_b measured between two surfaces of another material b for any set of liquids. In any homologous series, for one kind of solid surface, $u = \beta - \alpha M$, where β is a parameter

depending upon the solid, α a parameter depending only upon the chemical series (paraffins, alcohols, etc.), M =molecular weight. If we have two different solids, a and b then have each independent friction values, and

$$u = \frac{1}{2}(\beta_1 + \beta_2) - \alpha M$$

We can therefore specify our limiting friction coefficient in terms of any suitable solid. Since there is much available data for glass, we have taken that as standard; it will also differ little from flint (pebble) as used in our milling experiments.

The coefficient of friction to give a mechanical comminution of cellulosic material, e. g., in a ball mill, with excess liquid, should not be less than .25, measured between glass and glass. It has likewise been found that contaminations adhering to the cellulose will affect the result by acting as lubricants, the extraction, therefore, by the liquid used, of waxes and fats from the surface of the cellulosic material is an important factor.

Furthermore, in the comminution of fibrous materials the wetting power of the liquid dispersent should be considered. Very high wetting may tend to aggregate the fibrous particles, but very low wetting power is also undesirable. Compatibly with this, we find that the best dispersents, due regard being taken of the frictional coefficients and instable compounds, are semi-polar bodies rather than highly polar and non-polar bodies. Thus the very slightly polar carbon tetrachloride is very little suited to mechanical dispersion, while highly polar salt solutions do indeed give mechanical dispersion, but with great hydration, as before mentioned.

Suitable liquid dispersents which we have found capable of rapidly and therefore economically producing a highly comminuted cellulosic material and which have a coefficient of greater than .25, include the aliphatic organic acids from formic to caprylic, the aliphatic organic alcohols from methyl alcohol to cetyl alcohol, the aliphatic esters of acetic acid from methyl acetate to amyl acetate, and the halogen substituted paraffins. The ketones, while they have the required frictional coefficient, are nevertheless not particularly suited for our purpose as they generally form on the cellulosic materials condensation products which render the use of this material for further acetylation undesirable.

As the exposed surface of the cellulosic material is increased, the reactivity particularly to oxygen and water is likewise increased. To diminish then the oxidation of the cellulosic ma-

terial which may result in a degraded cellulose and ultimately in a degraded cellulose ester, the cellulosic magma is ground in the presence of an inert gas, such as carbon dioxide or nitrogen and preferably in a closed system. It is likewise possible but somewhat more expensive, to inhibit the sensitivity of the comminuted cellulose to oxygen by adding to the comminuting mass autoxidants in small amounts,—pyrogallol, hydroquinone, bisulfite of soda, etc., and similar autoxidants are useful.

We prefer, however, to carry on the subdivision of the cellulose in the presence of an inert gas due to the economical advantages it affords.

In the comminution of long fibered material the power consumption is rather high and we have found that it may be much reduced if the fiber be subjected to a preliminary shortening in a beating machine, using a close set tackle and avoiding hydration, i. e., conditions giving a very free half-stock. This preliminary shortened material may then be dehydrated with a suitable organic liquid e. g. methyl or ethyl alcohol which may be the liquid dispersent later used for the complete comminution of the cellulosic material.

As the comminution of the cellulose is carried beyond a certain stage in the presence of these dispersents, the cellulosic magma becomes less viscous and ultimately reaches a high degree of fluidity whereby the whole may be readily pumped or moved by gravity to the various subsequent treatments to which it may be subjected. This greatly facilitates the handling problems and results in material economies. This comminuted cellulose likewise, if a dispersing medium such as acetic acid be used, may be preacetylated to as high as 39% acetyl value even at room temperatures providing the mass be substantially dehydrated. The amount of acetyl which will be found to have combined with the cellulose will be inversely proportional to the moisture content of the magma.

The grinding may be carried out in a variety of mills suitable for wet grinding, ball and tube mills, disc mills and colloid mills. There may be obtained in this way comminutions of cellulosic materials ranging from impalpable powders to pulverulent materials of slightly fibrous character, substantially without chemical degradation and of value particularly in processes of esterification of cellulose, owing to the uniformity and homogenization possible, as well as materials suitable as fillers for various plastics.

The use of this comminuted material greatly increases the ease of esterification and particularly acetylation and correspondingly reduces the time and amount of chemical pretreatment of the cellulose. This comminution may be advantageously combined either with the chemical pretreatment of the cellulose and with the subsequent process of acetylation, or with an initial process of preacetylation (or partial acetylation) in which only a small percentage of acetyl is combined with the cellulose followed by or continued by a process of complete acetylation of the cellulose to a cellulose triacetate which contains approximately 44.8% acetyl.

The operation of the pretreatment or acetylating process with the employment of this type of cellulosic material may be conducted at a low or moderate temperature whereby ultimate chemical decomposition and degradation of the cellulose is avoided, and furthermore the necessity of cooling the acetylation mixture after pretreatment is eliminated. An improvement in quality of the resulting cellulose acetate with a notable

freedom from "grain" and imperfectly acetylated fibers is attained. The hydrolysis of the cellulose ester, such as the chloroform soluble cellulose acetate to the acetone soluble product may be continued in the same mill in which the pretreatment and the acetylation has been carried out and under similar operating conditions, with greater uniformity of action for low concentrations of the hydrolyst (aqueous mineral acid or its equivalent) and thereby producing a superior product.

The use of peptizers such as zinc chloride is well known and we have found that their use during the grinding operation in conjunction with the dispersent liquid aid considerably in many instances in the subdivision of the cellulosic material. As a number of these peptizers are likewise catalysts for the acetylation of cellulosic material particularly to cellulose acetate, their presence in the cellulose is not detrimental to its further esterification treatment and therefore need not generally be removed prior to such treatment. Other peptizers which we have found desirable are the mineral acids and particularly sulfuric acid.

We shall now give several examples for carrying out our process but it shall be understood that we are not to be limited by the details therein given except as indicated in the appended claims.

100 parts of cotton linters containing 2% moisture may be ground for 72 hours in a solution containing 3000 parts of acetic acid 99.5% and 75 parts of anhydrous zinc chloride at a temperature of 68° F. The cellulose is thereby very finely comminuted. The excess liquid is pressed off and can be reused in another comminution. 100 parts of this ground cellulose may then be treated with 550 parts of acetic acid, two parts of sulfuric acid, 5½ parts of zinc chloride and 180 parts of acetic anhydride. After treatment at 120° F. for 2½ hours a cellulose acetate containing 45.2% acetyl is obtained.

To 100 parts of cotton linters containing 2% water, 1000 parts of acetic acid of 99.5% strength, 39.5 parts of acetic anhydride 99.5% strength and 1.8 grams of sulfuric acid are added. The acetic anhydride is sufficient to combine with the moisture present in the resulting solution to form a solution containing merely anhydrous acetic acid and sulfuric acid. After grinding for four hours at 68° F. the ground product contains 9.65% acetyl. By a continuation of the reaction for sometime longer with a much more powerful grinding action a cellulosic material containing 30.1% acetyl results. This material, upon the addition of 1000 parts of acetic acid, .9 part of sulfuric acid and 100 parts of acetic anhydride may be completely acetylated to 44.7% acetyl in 6 hours at a temperature of 120° F.

To more fully describe the practical workings of our process the following description is given,—the cellulosic materials being treated in three stages. In the first stage the cotton linters, wood cellulose pulp, jute or similar materials are soaked with the liquid dispersent as acetic acid containing, if desired, from ½ to 1% or more of the peptizer; from 3 to 4 parts of the liquid are taken for 1 part of the cellulose and the mass turned over for one to two hours in an internal mixer such as a heavy dough mixer type. This treatment effects a preliminary breakdown of the fiber structure sufficient to break up the felted or matted mass and give mobile fluid. The smooth mass is then broken out with a disinte-

grating drum with spikes to smaller lumps and these lumps broken down to crumbs of $\frac{1}{8}$ to $\frac{1}{4}$ inch in diameter in a disintegrating hammer mill or drag mill. The weakening effect of the liquid dispersant and the peptizer, if used, permitting the material to be handled like peat or other moist fibrous material of low fibrous strength. In the second stage the material is now brought into a grinding mill at a 20 to 40% solid to liquid ratio. Sufficient acetic anhydride may be added to just take care of the water in the acetic acid and the cellulose, if a strongly pre-acetylated cellulose is required. This grinding may be effected either in a high speed colloid mill with recirculator or in ball or tube mills, preferably rubber lined to prevent corrosion. In this stage, lasting about two hours, the material is finally ground to disappearance of fibers. The cellulose may be here acetylated to contain as much as 27% acetyl. It is desirable that the preliminary acetylation be not conducted much beyond this percentage or a solubility of some of the cellulose acetate in the acetic acid solution will result.

In the third stage the fluid mixture is run through a separator, preferably some type of continuous centrifugal separator. The moist preacetylated cellulose is treated with acetic anhydride and acetic acid and if required with more of the peptizer which in this case will be the catalyst and the resulting mass acetylated at a temperature of 90 to 120° F. until the triacetyl cellulose is obtained. We have found that it is possible to acetylate the cellulose, which at this stage contains approximately 25% acetyl, by the addition to 100 parts of the cellulose of only 120 to 150 parts of anhydride.

Any of the usual types of disintegrating apparatus may be effectively used in carrying out our process while stable equivalents of the liquid dispersant with or without the addition of the peptizer may be employed for a successful operation of our process without in any way departing from this invention or sacrificing any of the advantages that may be derived therefrom.

What we claim as our invention and desire to be secured by Letters Patent of the United States is:

1. A process for the comminution of cellulose which comprises comminution of the material in the presence of acetic acid in which it is insoluble.

2. A process for the comminution of cellulose which comprises comminution of the material in the presence of an inert gas and a liquid dispersant selected from the compounds included in the groups consisting of stable aliphatic organic acids and alcohols, aliphatic esters of acetic acid, and halogen substituted paraffins having frictional coefficients greater than .25.

3. A process for the comminution of cellulose which comprises comminution of the material in a closed system containing carbon dioxide and a liquid dispersant selected from the compounds included in the groups consisting of stable aliphatic organic acids and alcohols, aliphatic esters of acetic acid, and halogen substituted paraffins having frictional coefficients greater than .25.

4. A process for the comminution of cellulose which comprises the comminution of the material in the presence of an inert gas and acetic acid.

5. A process for the comminution of cellulose which comprises comminution of the material in the presence of an inert gas and a stable, liquid dispersant having a coefficient of friction greater than .25.

6. A process for the comminution of cellulose which comprises comminution of the material in the presence of an inert gas and a stable, semi-polar, liquid dispersant having a coefficient of friction greater than .25.

7. A process for the comminution of cellulose which comprises comminution of the material in the presence of a liquid dispersant in which it is insoluble selected from the compounds included in the groups consisting of stable aliphatic organic acids and alcohols, aliphatic esters of acetic acid, and halogen substituted paraffins having frictional coefficients greater than .25, and an acid peptizer.

8. A process for the comminution of cellulose which comprises comminution of the material in the presence of a liquid dispersant in which it is insoluble selected from the compounds included in the groups consisting of stable aliphatic organic acids and alcohols, aliphatic esters of acetic acid, and halogen substituted paraffins having frictional coefficients greater than .25, and sulfuric acid.

9. A process for the comminution of cellulose which comprises comminution of the material in the presence of acetic acid and sulfuric acid in which mixture the cellulose is insoluble.

10. A process for the comminution of cellulose which comprises subjecting the cellulosic material to a preliminary shortening without hydration, dehydrating the pretreated cellulose with a stable, liquid dispersant having a coefficient of friction greater than .25 and subsequently comminuting the cellulose in a closed system containing an inert gas, a dispersant, and a peptizer.

11. A process for the comminution of cellulose which comprises comminution of the dehydrated material in the presence of an inert gas, acetic acid and sulfuric acid and subsequently acetylating the comminuted and pretreated material.

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