The present invention relates to reactive treatments of cellulose. It has particular reference to the esterification as by nitrating of fibers of cellulose, such as wood fibers. Although wood fibers are classified generally into long fibers and short fibers, I do not refer in this invention to these subdivisions of wood fibers, but aim to distinguish between the fibers of natural cotton cellulose and the fibers of chemically prepared and isolated cellulose, as from wood.

Cotton is the common form of cellulose which is nitrated, and its fibers are distinctive. Cotton fibers, such as linters, is nitrated with a mixture of sulphuric acid and nitric acid. Excess acid and the resultant treated fibers are quickly separated in a centrifuge. Although the chemistry of the process is or may be the same for nitrating suitable chemical wood pulp, which also is cellulose, it has been found that there are many difficulties encountered by the mere substitution of wood pulp fibers for cotton fibers. The present invention aims to overcome these difficulties.

Cotton by nature easily mats into a fluff or ball, or whatever size or form of mat is permitted, in such a way that the mat is highly porous and absorbent. For the purpose of this invention it may be described as presenting open channels to its interior, so that esterifying acid may penetrate to the interior as a liquid flowing in the channel as distinguished from diffusion of liquid through a mass of more or less compressed fibers or through capillary channels between or within fibers. In the case of fibers, especially in nitrification, especially in nitrification, and particularly where the process is carried out in a relatively short time, it is essential that all the fibers be esterified and be uniformly esterified. Hence it is essential that the interior of fibrous balls or mats be quickly reached by acid. Where the exterior fibers of any such mass are effective to bar a flowing access of acid to the interior, the process of transfer through the obstructing exterior fibers may wholly or partly exhaust the active strength of the acid, and an incompletely esterified or an unesterified product is obtained on the inferior. Although a large part, such as 95%, may be properly esterified, a slight residue of even slightly under-treated fibers, will manifest itself as undissolved or partially dissolved fibers, or as cloudiness in a solution of the mass. These defective features are not always manifest in the product and it is impossible or difficult to remove these defects from the product. Hence, the defect must be prevented at the source.

In the application of Walter F. Hoffman, and Roy H. Hell, Serial No. 601,566, filed March 28, 1932, substantially concurrently herewith, there is described an improvement in the centrifuge basket which overcomes the difficulties in that phase of nitrating wood pulp. In the application of William Courtney Wilson, Serial No. 184,435, filed April 16, 1937, now Patent No. 1,985,162, issued September 5, 1934, there is described a process of preparing, as by shredding, ordinary wood pulp, or lap board, for nitration. In the application of William Courtney Wilson, Serial No. 119,996, filed July 1, 1926, now Patent No. 1,883,215, there is described a process of nitrating chemical wood pulp. The present invention relates to the earlier stages of the entire process, and in particular to the preparation of the pulp to condition it for nitration or other reaction. It relates to the manner of drying pulp or fibers from the wet process of chemical manufacture of cellulose from wood or other treatment of any wet cellulose comparable in certain properties to wood pulp fibers. From the following description it will be apparent that the process is not limited to chemical cellulose, or to chemical wood pulp, or to short fibers, but is applicable to natural cellulose, such as cotton, whether of long or short fibers, and applicable to regenerated cellulose in various forms, such as films. However, its major advantages are greatest when applied to fibers which mat easily and especially to chemical wood pulp.
For understanding the present invention there must be recognized (1) certain distinctive properties of the fibers, or perhaps it may better be stated to be the average property of an aggregation of fibers, and (2) certain distinctive properties of a reactant fluid in its action upon said fibers. Cotton for example does not mat easily, and little difficulty is experienced in nitratizing cotton fibers. Cotton is a fiber which grows in a twist or twist in it, by reason of which it is more or less kinky. Fibers from other vegetation, such as wood grow in bundles, and are straight. They may be released by chemical process, or fibrated, into the individual fibers, lacking the kinks of cotton. By reason of the chemical processes of isolation they become highly flexible. Hence, it may be comprehended why they may act differently in aggregate form, than natural cotton fibers.

Cotton on the other hand acts differently in acetylatizing baths than in nitration baths (see U. S. Patent No. 1,544,941). Because acetylatizing baths gelatinize cellulose prior to dissolving the ultimate product of reaction, there is a tendency for the gelatinized cellulose to form a dam between liquid and fiber, thereby preventing reaction on part of the fiber. This may produce non-uniform reaction and a variable product, which is a mixture of products having different degree of acetylation. See made small pills or aggregates of his fibers.

The foregoing establishes that cotton fiber acts differently in nitration than in acetylation. Chemical wood fiber and cotton act differently in nitration. But in the ultimate analyses of these differences, the physical form of the cellulose plays an important part. By reason of the present invention of the difficulty is avoided for any fiber and for any process by control of the physical form.

Practically all commercially available forms of wood pulp are either wet, or are dried by evaporating moisture from wet forms. Usually, it is supplied in wet or dry lap board. Dry lap board, or any other form of such dried pulp may be mechanically disintegrated, but great care must be taken in doing this, and in treating and handling the product to prevent the formation of an indefinite amount of dust. Mechanical disintegration creates a certain percentage of cut fibers or dust which may become lost in the process, and it is difficult to completely disintegrate by mechanical means. Cotton fiber also has been similarly treated. The general object of the present invention is to treat wet cellulose so that its physical characteristics are changed advantageously for nitration and other reactive treatments.

A particular object of the invention is the removal of water from wet cellulose, such as fibers, by a dehydrating agent, as distinguished from evaporation of water therefrom, followed by reaction with fibers so dried.

A particular object is the replacement of water in the fiber with a liquid of different character, such as benzol, alcohol or acetone, followed by removal of the replacing liquid from the fiber, as steps preceding reaction with said fiber.

A further object of the invention is the replacement of water of unbeaten fiber, or fiber which has not been specially treated, as by beating, to hydrate the same to prepare fiber for chemical reaction.

Various other objects and advantages of the invention will appear from the following description and explanation.

I have discovered that one characteristic of dried water-wet fiber which makes it mat and compact disadvantageously is a feature which is desired in paper making, and which may be eliminated advantageously for chemical treatments, such as esterification processes, with water, or hydrates, and when the water is evaporated, the swollen fiber shrinks. The swelling and the shrinkage is greater according to the amount of hydrated or so-called gelatinized cellulose that is present. Fibers for paper-making are usually beaten to effect this condition, and the fiber is thus made more open and porous. By using unbeaten fiber, and avoiding as far as possible processes or treatments which so affect fibers, the fiber can be retained in a more natural condition, and more comparable to cotton. In the process of isolating cellulose from wood, a certain degree of hydration may be effected chemically, but this is to be distinguished from mechanical hydration, and special chemical treatments which effect a mercerizing action on the fibers. When a fiber is wet with water it has more character of a fibrous gel than when dry or when wet with a liquid for which it has no special affinity, or toward which it is lyophobic. Water-wet fibers dried in contact with each other are coherent to each other, and shrink and bind each other. Hence they are separated with great difficulty. They mat closer and pack tightly, as exemplified in making paper.

Alcohol-wet fibers do not do this, and therefore, when fibers wet with a liquid, like alcohol, and different from water, are dried they are differently related to each other in a mass. Under a microscope up to 100 diameters no characteristic difference is visible between a fiber dried from being wet with alcohol and a fiber dried from being wet with water. However, if each of such dried fibers is wet with water both can be seen to swell under a microscope of 70 diameters. If dried fibers under a microscope are wet with alcohol, and observed while the alcohol is diluted with water, the fibers may be seen to swell as they take up water.

Although no difference is apparent to the eye in microscopic examination of the two types of fibers, there is a distinct difference in properties which is manifest in assembling the fibers into a mass. The dried water-wet fibers appear stiffer and harsher and mat together on being compressed. The dried hydrated cellulose apparently is a binding agent in the fiber. The dried alcohol-wet fibers are soft and flexible and exhibit much less tendency to adhere, pack and mat on being compressed. A compact mass of such fibers is more readily loosened into a fluffy mass than is a compacted mass of dried water-wet fibers. This makes it much easier to prepare, compress, ship, and subsequently loosen compacted fibers for an esterification or other reactive process.

In the present invention I aim to use in any reactive process, such as esterification, like nitration, fibers which have been dried in the presence of each other from a condition in which they lack water, or are wet with a liquid having no affinity or swelling for the fiber is comparable to water. Preferably, I use a liquid which is miscible with water, so that in wetting water-containing fibers with the liquid, the liquid extracts water. The removal of water by replacement may be carried out in numerous ways. Reference is made to the

Example I

Unbeaten bleached sulphite pulp, such as that ordinarily fed into a beater to prepare it for making pulp, both alone and on a filter, by suspending the pulp in water and drawing off the water through the filter. Successive portions of alcohol, such as commercial denatured alcohol, are poured over the pad, and drawn through it until water is displaced. Using denatured alcohol of a kind which will take on a much greater volume of water, before the denaturant is precipitated out is satisfactory when applied until the filtrate from the pulp is clear and free from precipitated denaturant. Absolute alcohol may be used to assure complete removal of water.

The mat made in a filter by this process is characteristically different from a mat made from water-wet fibers. A dried water-formed filter mat is like an ordinary piece of paper. It is harsh, flat, and the fibers are tightly bound to each other. So few fibers end project upwardly from the surface that the surface has a harsh feel. A dried alcohol-formed mat is soft and velvety and the fibers are loosely related and easily pulled apart. Many free ends of fiber project from the surface giving it a soft velvety feel.

If two mats, one from water and one from alcohol are folded and creased with the fingers, and the creases are examined with a lower power (4 times) hand magnifying glass, the ridge of the water felted mat is sharp and clear, like any piece of paper. The ridge of the alcohol mat is not as sharp a crease and is covered with a fringe of free ends of fibers.

The difference in character of the massed fibers is due at least in part to the mutual affinity between the fiber and the liquid it contains. The differences in affinity is due to different liquids or different fibers become manifest as the liquid is removed to form dry fibers. The fact that the affinity is responsible for this is exemplified by the following experiment which shows that it is not wholly the liquid property but the fiber property, both related by the affinity of the fiber to the liquid.

Nitrated cellulose fibers of wood are suspended in water and felted on a filter like any paper test sheet is made in the paper mills. The resulting sheet is not thin and velvety and of a most delicate character because of the lack of adherence of one fiber to another. Nitrocellulose is a hydrophobe and cellulose fibers are a hydrophilic. This measure of affinity is a sort of measure of the extent to which the fibers adhere when matted from a liquid. If alcohol is used to mat nitrated cellulose fibers having an affinity for alcohol the sheet is harsh and unlike the water-matted sheet.

The foregoing shows that with the two types of liquid, alcohol and water, nitrated cellulose fibers give results which are the reverse of results which cellulose fibers give with said two types of liquid.

After making a cellulose mat from alcohol, not only does the mat, the fibers mechanically in the air or with heat without any apparent difference in the result. It has been dried at 60°--70° C. The cellulose mat may be easily disintegrated with the fingers in striking contrast to the difficulty in so doing with a water-felted cellulose mat. This mat, being a more uniform process and product results. It is not necessary to use the fibers in any special form, such as a bulk of loose fibers, for they may be used in a mat as described in the application of Walter F. Hoffman, Serial No. 691,711, filed March 28, 1932, substantially concurrently herewith.

Although I have referred particularly to fibers of mat or of practically loose non-matting individual fibers. The shredded mat is then nitrated for example, by taking 120 kilograms of fiber to 2900 liters of nitric acid at 55° C., according to the process of the Wilson application Serial. No. 119,965. Any nitrating acid may be used, but that described by Wilson is especially adapted for a quick nitration, in which type of process the advantages of the present invention are most pronounced. After stabilizing the nitrated product in any usual way, the product may be dehydrated with alcohol and dissolved in butyl acetate, in a solvent, to form a 5% solution. A clear solution, lacking cloudiness and fibers, is obtained, indicating complete and sufficiently uniform form nitration to yield a high grade commercial nitrocellulose.

Example II

Unbeaten chemical wood pulp having a high content of alpha cellulose, and known as an "alpha cellulose pulp" was matted from water, and another sample was matted from alcohol. The two mats were then shredded to form substantially individual fibers. Similar quantities (bone dry bases) of each pulp in air dried condition, were employed in comparative acetylations. The following procedure is illustrative of an acetylation process.

5 grams of pulp is added to a mixture 200 cc. of glacial acetic acid, 60 cc. of acetic anhydride, and 1 cc. of concentrated sulphuric acid. The reaction mass may be agitated from time to time for a period of 24 hours at about 25° C. By this time the reaction is so complete that all the fiber is dissolved. The liquid is then poured in a thin stream into 5 liters of water, in which the cellulose acetate is precipitated. It is then filtered and washed free from residual acid. The filter cake may be dried, as at 70° C.

The alcohol-dried pulp gives a higher weight yield than the water-dried pulp by over 10%. In the process of preparing the pulps the water-matted air-dried pulp retains practically 10% moisture, and/or as hydrated cellulose. The alcohol dried pulp lacks the hydrated character. The reaction rate is usually greater in using the alcohol-dried fiber.

Other types of pulp may be employed and the shredded form is not an essential form. For example, a bleached cellulose pulp made by cooking wood with a solution of neutral type of cooking liquor, such as a mixture of sodium sulphate and sodium carbonate, (according to the process of Textor Serial No. 135,929, filed September 10, 1920) may be used in alcohol dried form. Such pulp may be felted from alcohol to form when air dried a mat which is about one-half inch thick. Fragmentary pieces of the mat in substantially the form and size, or bulk of 1/2 inch cubes, are as readily acetylated as is the shredded form, and the yield as substantially the same as from the shredded form and higher than the water-felted pulp. It is believed that the dehydrated form of the cellulose minimizes the gelatinization of the fibers, and hastens acetylation and dissolution. The time for acetylation may be thus shortened, and a more uniform process and product results. It is not necessary to use the fibers in any special form, such as a bulk of loose fibers, for they may be used in a mat as described in the application of Walter F. Hoffman, Serial No. 691,711, filed March 28, 1932, substantially concurrently herewith.
of cellulose, such as those derived from nature, as from wood, I aim to include natural cotton fibers, and also artificial fibers of cellulose, such as regenerated cellulose, like artificial silk. Such regenerated forms may be treated according to the process herein described, to remove the effects of hydration and to put the cellulose into a different physical form for the subsequent chemical reaction. These advantages, however, appear greatest when fibers like wood pulp are used, and when those fibers are unbeaten and unmercerized, so as to retain as near as possible a natural fiber form.

The nitration is an example of a process wherein the fibers retain their physical microscopic identity. The acetylation is an example of a process in which the fibers lose that identity. In both types there are advantages to be gained because of the physical character of the fiber employed. The invention therefore is not to be considered as limited to these processes but contemplates other reactive fluids, especially liquids, where penetration of the fiber is essential or incidental to reaction with the substance of the fiber. Such other uses and modifications of the invention are herein contemplated as fall within the scope of the accompanying claims.

I claim:

1. The process of making a cellulose derivative from cellulose fibers which comprises treating unbeaten non-mercerized water-wet cellulose fibers with a dehydrating liquid to remove water therefrom, removing all of the dehydrating liquid from the fibers, separating the fibers into a loose fluffy mass, and subjecting the fluffy mass to the action of an agent reactive upon cellulose.

2. The process of making a cellulose derivative from cellulose fibers which comprises treating unbeaten non-mercerized water-wet cellulose fibers with a dehydrating liquid having less affinity for cellulose than water, removing all of the said dehydrating liquid from the fibers, separating the fibers into a loose fluffy mass, and subjecting the loose fluffy mass to the action of an agent reactive upon cellulose.

3. The process of making a cellulose derivative from cellulose fibers which comprises treating water-wet fibers with a liquid capable of removing water therefrom and of replacing the water with the liquid, filtering the liquid from the fibers to form a mat, drying residual liquid from the mat, shredding the mat to form a loose fluffy mass of fibers, and subjecting the loose fluffy mass to the action of an agent reactive upon cellulose.

4. The process of making a cellulose derivative from cellulose fibers which comprises treating unbeaten non-mercerized water-wet fibers with alcohol to remove water therefrom and to leave fibers containing alcohol, removing excess liquid alcohol by a filtration process, forming a mat, drying out the residual alcohol in the mat, shredding the mat into a loose fluffy mass, and subjecting the mass to the action of an esterifying liquid.

5. The process of making a cellulose ester from cellulose fibers which comprises treating water-wet fibers with a dehydrating liquid having less affinity for cellulose than water, removing all of said dehydrating liquid from the fibers, separating the fibers into a loose fluffy mass, and subjecting the loose fluffy mass to the action of an esterifying liquid.

6. The process of making a cellulose ester from cellulose fibers which comprises treating water-wet fibers with alcohol to remove water therefrom and of replacing the water with the liquid, filtering the liquid from the fibers to form a mat, drying residual liquid from the mat, shredding the mat to form a loose fluffy mass of fibers, and subjecting the loose fluffy mass to the action of an esterifying liquid.

7. The process of making a cellulose ester from cellulose fibers which comprises treating water-wet fibers with a liquid capable of removing water therefrom and of replacing the water with the liquid, filtering the liquid from the fibers to form a mat, drying residual liquid from the mat, shredding the mat to form a loose fluffy mass of fibers, and subjecting the loose fluffy mass to the action of an esterifying liquid.

8. The process of making a cellulose ester from cellulose fibers which comprises treating water-wet fibers with alcohol to remove water therefrom and to leave fibers containing alcohol, removing excess liquid alcohol by a filtration process, forming a mat, drying out the residual alcohol in the mat, shredding the mat into a loose fluffy mass, and subjecting the mass to the action of an esterifying liquid.

9. The process of making a cellulose ester from cellulose fibers which comprises treating water-wet fibers with alcohol to remove water therefrom and to leave fibers containing alcohol, removing excess liquid alcohol by a filtration process forming a mat, drying out the residual alcohol in the mat, shredding the mat into a loose fluffy mass, and subjecting the mass to the action of an esterifying liquid.

10. The process of making a cellulose ester from cellulose fibers which comprises treating water-wet fibers with alcohol to remove water therefrom and to leave fibers containing alcohol, removing excess liquid alcohol by a filtration process forming a mat, drying out the residual alcohol in the mat, shredding the mat into a loose fluffy mass, and subjecting the mass to the action of an acetylation agent.

11. The process of making a cellulose derivative from cellulose fibers which comprises treating unbeaten non-mercerized water-wet fibers with a liquid capable of removing water from the fibers and of replacing the water by itself, removing all of the liquid from the fibers, gathering the fibers into a loose fluffy mass, and subjecting the mass to the action of an agent reactive upon cellulose.

12. The process of making a cellulose ester from cellulose fibers which comprises treating water-wet fibers with a liquid capable of removing water from the fibers and of replacing the water by itself, removing all of the liquid from the fibers, gathering the fibers into a loose fluffy mass, and subjecting the mass to the action of an esterifying liquid.

13. The process of making a cellulose ester from cellulose fibers which comprises treating water-wet fibers with a liquid capable of removing water from the fibers and of replacing the water by itself, removing all of the liquid from the fibers, gathering the fibers into a loose fluffy mass, and subjecting the mass to the action of an esterifying liquid.
mass, and subjecting the mass to the action of an acetylating agent.

15. The process of making a cellulose derivative from cellulose fibers which comprises forming with water a wet mat of unbeaten non-mercerized cellulose fiber, passing through the mat a dehydrating agent which carries the water away from the mat, removing residual dehydrating agent from the mat, disintegrating the mat into a loose fluffy mass of fibers, and subjecting the mass to the action of an agent reactive on cellulose.

16. The process of making a cellulose derivative from fibers which comprises subjecting a water-wet mass of unbeaten non-mercerized cellulose fibers to a dehydrating agent to remove water from the fibers and to impregnate the fibers with said agent, removing all of the said agent from the fibers, forming the fibers into a loose fluffy mass, and subjecting the mass of fibers to the action of an agent reactive with cellulose.

17. The process of making a cellulose derivative which comprises displacing water in unbeaten non-mercerized wet-cellulose by a non-dehydrating agent, removing all of said agent, and subjecting the cellulose to the action of a liquid agent reactive upon cellulose.

18. The process of making a cellulose derivative from cellulose fibers which comprises immersing unbeaten non-mercerized water-wet cellulose fibers in a liquid to which the cellulose is lyophobic, removing water from the fibers in the presence of said liquid, removing all of said liquid from the fibers, separating the fibers into a fluffy mass, and subjecting the fluffy mass to the action of an agent reactive upon cellulose.

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