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PREPARATION OF NITROCELLULOSE

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This invention relates to the preparation of nitrocellulose characterized by its low solution viscosity, that is, the capacity of being dissolved in suitable solvent media to form solutions of low viscosity. More particularly, it deals with the preparation of nitrocellulose of this character as a product resulting directly from the nitrating reaction and the raw material used therefor. In other words, rather than involving the chemical treatment of the explosive and highly inflammable nitrocellulose product to bring it to the desired low solution viscosity, as is generally the practice, the present invention has for its objective the transformation of the cellulose fiber used as parent or raw material so that it will yield immediately upon nitration a nitrocellulose product of the desired low solution viscosity and useful in the manufacture of lacquers, films, artificial silk, and other nitrocellulose products.

In accordance with the present invention, cellulose fiber is treated in interfelted sheet form with a solution-viscosity-lowering reagent and, after the desired transformation in the solution viscosity of the fiber has been effected, the interfelted or sheeted fiber is shredded and the shreds nitrated to form directly the desired low viscosity nitrocellulose product. While not limited thereto, the solution-viscosity-lowering reagent preferably employed in accordance with the present invention is a dilute solution of such strong mineral acids as hydrochloric, sulphuric, and nitric, as such acid solutions, although comparatively inexpensive, are especially effective in bringing about the desired transformation of the cellulose fiber. I am aware of the fact that it has been proposed to treat cellulose fiber in bulk condition or as an aqueous suspension with mineral acid solution prior to nitration, but, when cellulose fiber is thus treated, there is a serious loss of cellulose by reason of the fact that fine fibers and fiber fragments present in the stock, more especially after the stock has undergone the hydrolyzing and accompanying fiber-shortening action of the mineral acid solution, cannot be retained but are carried away by the mineral acid solution drained from the stock and/or the wash water employed for washing the stock. In the practice of the present invention, however, notwithstanding the fact that the fiber units within the sheets may be reduced in size to a greater or less degree according to the nature of the viscosity-lowering treatment effected thereupon, the fibers, being well interfelted, hold together and keep entrained or locked in the sheets the fine fibers and fiber fragments, in consequence of which the sheets can be washed and dried or directly dried without loss of cellulose. The dried sheets can then be shredded and the shreds nitrated in accordance with the present invention to produce with high yield the desired low viscosity nitrocellulose product, as the shreds comprise the fine fibers and fiber fragments which, by virtue of their exceedingly low solution viscosity, contribute importantly toward minimizing the solution viscosity of the nitrated product.

The viscosity-lowering treatment of the present invention may be carried out in various ways and upon sheets of various dimensions and containing various kinds of cellulose fiber. However, I prefer to work with wood pulp sheets, preferably such as are of high alpha cellulose content and otherwise suitable for use in the production of nitrocellulose, as such sheets offer an important practical advantage when used as raw material. This advantage resides in the fact that chemical wood pulp mills are generally equipped to market, and in fact usually do market, unbeaten wood pulp in the form of so-called drier sheets, which are produced by passing the processed wood pulp as an aqueous suspension over pulp dryers sometimes built as large units capable of handling large amounts of pulp, say, 200 tons or more of dry fiber per day. Such sheets are currently being sold, for example, for conversion into artificial silk by the viscose-rayon process, wherein they are handled as such with facility in making so-called alkali-cellulose. A specific example of procedure falling within the purview of the present invention may be carried out substantially as follows. Drier sheets of white, refined wood pulp of high alpha cellulose content, say, of an alpha cellulose content of at least about 93%, and of a thickness of, say, about 0.035 inch, are suspended on a rack in a 1% HCl solution at 95° C. for six hours. They are then drained free of excess acid and are washed to remove residual acid contained therein. The washed sheets are then partially dewatered, as by squeezing between rolls, whereupon they are dried in an atmosphere of warm air. The dried sheets are then shredded in a suitable machine, preferably a hammermill, as such latter machine is rugged and comparatively inexpensive and has a high output of shredded product of high bulkiness or voluminosity. Of course, shredding of the sheets may be performed by other than impact machines, for instance, by carding or similar machines which pick or tease out the fibers from the sheets. It is distinctly desirable, however, that the sheets be shredded in the presence of a controlled amount of moisture, as described in Patent No. 1,880,052, issued September 27, 1932, to Benjamin G. Hoos and myself, as shredding under such conditions results in a shredded product substantially free from hard fiber clumps and fiber dust and hence giving the best results upon nitration. When shredding is performed in the presence of moisture, the shredded product is preferably dried preparatory to nitration. The substantially dry, shredded product is then nitrated as in the usual mixed nitrating acids or in a nitrating mixture rich in nitrating acid and otherwise conformable to the disclosure of my Patent No. 1,914,302, dated June 13, 1933.

Instead of using a solution of acid in treating the sheets as described in the foregoing example, I may use acid fumes or vapors, preferably fumes or vapors of volatile mineral acids such as hydrochloric, or nitric acids admixed, if desired, with water vapor, steam or air. The exposure of the sheets to the acid fumes may be carried out for, say, one to two or more hours; and the atmosphere of acid fumes may be at a temperature ranging from room temperature to 100° C. or even higher. Indeed, the acid and temperature conditions of the treatment with the acid fumes are subject to wide variation, depending upon the solution-viscosity quality desired in the finished nitrocellulose. The acid fumes readily penetrate into and throughout the sheets so as to effect a substantial uniform chemical modification thereof. After the sheets have undergone the desired transformation in the atmosphere of acid fumes, they may be washed, dried, shredded, and the shreds nitrated as hereinbefore described; or, the step of washing the fumed sheets may be omitted from the sequence, particularly when nitric acid fumes alone are used as the solution-viscosity-reducing agent.

In lieu of using acid solutions or acid fumes in the treatment of the sheets, I may use solutions of oxidizing agents, such as sodium or calcium hypochlorite, potassium permanganate, or ammonium persulphate, or mercerizing solutions containing, if desired, one or more of such oxidizing agents, as oxidizing agents can be used in concentration and under time and temperature conditions to effect also a marked lowering of the solution viscosity of cellulose fiber. A suitable oxidizing agent, such as any one of those mentioned, may also be added to an acid reagent with which the sheets are to be treated. The oxidizing reagent employed for reducing the solution viscosity of the fiber may, however, be nonacid, the desired effect being produced, for example, with neutral or alkaline solutions of potassium permanganate. When sheets are treated with mercerizing solutions in accordance with the present invention, they are washed after such treatment, and, if desired, then treated with dilute mineral acid solution and preferably again washed to remove acid residues, whereupon the sheets are dried, shredded, and the shreds nitrated.

In making nitrocellulose of exceedingly low solution viscosity, for instance, nitrocellulose of the ½-second variety or lower, it is of advantage to combine two or more treatments of the fiber, as one may realize a cumulative effect of such treatments. A combination of treatments which has been found especially effective and advantageous in reducing markedly the solution viscosity of cellulose fiber is a mercerization of the fiber followed by the treatment of the fiber in sheet form with one of the hydrolyzing mineral acid reagents or one of the oxidizing agents hereinbefore mentioned, preferably a dilute aqueous solution of mineral acid, while maintaining intact the sheeted form of the fiber. The mercerization of the fiber, as well as its subsequent hydrolysis with dilute mineral acid solutions is preferably effected with the fiber in the form of drier sheets, not only for the reasons hereinbefore noted but further because it is much more difficult to make uniform sheets of mercerized fiber than of unmercerized fiber owing to the curly nature of the former, its exceedingly high freeness, and its pronounced tendency to gather into clumps. Further, when pulp is mercerized in sheet form, excess alkali may be readily removed and recovered therefrom by pressing, and residual alkali is easily washed therefrom, whereas it is a comparatively difficult matter to remove alkali from cellulose fiber mercerized in bulk, as in such latter case the mass is highly gelatinous and does not readily release entrapped alkali when subjected to draining, squeezing, or washing operations. Also, sheets of unmercerized pulp are much stronger and more tenacious than sheets of pulp mercerized in bulk. Again, the mercerization of a drier sheet toughens it so that its integrity or capacity for holding together during the subsequent hydrolytic treatment is enhanced, particularly if the mercerized sheet is steeped in hot water as opposed to cold water after the mercerizing solution has been drained off. A two-step treatment of cellulose along these lines, using drier sheets of the kind hereinbefore described as raw material, may be practiced substantially as follows. The drier sheets are initially steeped for one-quarter to four hours in an 18% caustic soda solution at 18° to 20° C. and the solution-soaked sheets are then pressed free of excess solution. Both these operations may be performed in a steeping press, such as is used in the viscose industry. The pressed, mercerized sheets containing residual mercerizing solution are in a firm intact condition. They may hence be plunged into a bath of preferably hot wash water in which they hold together entirely satisfactorily. Preferably after several changes of hot water in the bath, the water is drained off, and a 1% solution of hydrochloric acid at 90° to 95° C. is added to the sheets, in which solution the sheets are allowed to remain submersed for about one-quarter to two hours. The acid solution is then drained off and the sheets are again washed, preferably with hot water and with several changes of such water. The water-soaked sheets are then squeezed free of excess water and the resulting moist sheets are dried as on a rack in an atmosphere of warm air, whereupon the dried sheets are disintegrated into shreds preferably in the presence of a controlled amount of moisture, as hereinbefore described, the shreds dried, and finally nitrated to produce with good yield nitrocellulose of lower than ½-second viscosity and lending itself to dissolution in the usual nitrocellulose solvents to form solution of excellent water-white color and clarity.

In certain instances, it may be expedient to mercerize the pulp in bulk form and then to hydrolyze the mercerized pulp after it has been made up into sheets, as in such instance, too, the treatment of the mercerized fiber in sheet form makes possible the realization of the advantages hereinbefore noted. The mercerizing solutions may be applied at above room temperature in the treatment of the fiber, as I have found that reduction in solution viscosity of the fiber is favored by elevated temperature as well as by mercerization. I can thus take advantage of the effects of both mercerization and of heat in breaking down the size of the cellulose molecular aggregate and can hence secure better results than can be had through either effect alone. This combined effect of mercerization and heat may be realized by applying the hot mercerizing liquor either to bulk cellulose fiber or to fiber in the form of sheets. The fiber may be cotton linters, as well as wood pulp or cellulose fiber of other derivations. Ordinarily, mercerizations are carried on at room temperature or lower, since as the temperature of the caustic soda solution is raised, the concentration of caustic soda in solution must be increased in order to effect mercerization; but in view of my finding that a heated solution of caustic soda has a markedly enhanced effect on the reduction of the solution viscosity of the fiber, warm or hot mercerizing solutions may be advantageously applied to the fiber in combination with a subsequent hydrolytic treatment of the fiber. For instance, drier sheets of refined wood pulp may be steeped for four hours in a 37½% solution of caustic soda at 125° C. under atmospheric pressure conditions, as such a strong solution mercerizes at this high temperature. When sheets so mercerized are drained, washed with hot water, dried, shredded, and the shreds nitrated, as hereinbefore described, a good yield of high quality nitrocellulose of very low solution viscosity is obtained. When sheets so mercerized are washed, then steeped in a 1% hydrochloric acid solution for one hour at 90° C., then again washed, dried, shredded, and the shreds nitrated, as hereinbefore described, a good yield of high quality nitrocellulose of a solution viscosity much lower than ½-second is realized.

The mercerizing solution may be used at a temperature above the normal or atmospheric boiling point by heating it under confinement in a pressure vessel or digester, but in such case very highly concentrated caustic soda solutions are necessary to bring about mercerization. In order to avoid the necessity of using highly concentrated caustic soda solutions for mercerizing, a solution of, say, 18% caustic soda may first be used at room temperature or lower to effect mercerization of the fiber, and, after the fiber has been thoroughly saturated with the solution and mercerized, the solution may be heated considerably to produce a change of solution viscosity incident to a temperature far above the mercerizing temperature of the solution. As already indicated, the mercerizing solution may contain oxidizing agents such as hypochlorites, permanganates, or persulphates to promote a reduction in the solution viscosity of the fiber. The mercerizing solution may, on the other hand, contain reducing agents, such as sodium sulphide, or sodium sulphite. Before washing the mercerized sheets, they may be aged, as is done in the viscose-rayon industry, as ageing also fosters a lowering of the solution viscosity of the fiber. The subsequent hydrolyzing treatment may be performed on the fiber with various hydrolyzing media, including acid or acid salt solutions, acid fumes, hot water or water vapor under super-atmospheric pressure, and hot dilute solutions of mildly alkaline substance under superatmospheric pressure.

So far as concerns subject matter, this is a continuation-in-part of my application Serial No. 461,854, filed June 17, 1930, now Patent 2,029,547, issued Feb. 4, 1936, and is designed to cover the principles of the invention therein disclosed when the sheets, after the initial viscosity-lowering treatment, are shredded and nitration is performed on the dry shreds. The retention of the fines, that is the fine fibers and fiber fragments, is of great importance during the preparation or initial modification of the stock for nitration even though it is true, as set forth in the parent application, that for the very best results the fines must be saved throughout the entire process. However, in those instances when nitrating mills are equipped to nitrate shredded pulp, the process herein disclosed and specifically claimed is highly advantageous.

So far as I am aware, I am first to discover the value of treating cellulose fiber in interfelted sheet form, preparatory to nitration, with solution-viscosity-lowering reagents, such as the mineral acids, more particularly in dilute solution or vapor form, to realize the high effective solution-viscosity-lowering effect of such reagents without substantial loss of reduced fiber units resulting from such treatment. It so happens that the reagents most effective for reducing the solution viscosity of cellulose fiber, such as dilute solutions of mineral acids, also function to shorten the fiber units, and this is also true of such oxidizing agents as the hypochlorites, permanganates and persulphates, which, when used in amount or concentration and under time and temperature conditions to effect a marked reduction in the solution viscosity of cellulose fiber approaching that effected by dilute mineral acid solution, also embrittle and shorten fiber units to a point where they would be lost if treatment were effected on bulk fiber and the fiber washed in suspension or slush form. Owing to the lack of a satisfactory generic term covering both mineral acids and oxidizing agents, I shall in the appended claims define both these classes of chemicals as reagents that effect a marked lowering of the solution viscosity of cellulose fiber and a reduction of the size of cellulose fiber units.

I claim:—

1. In a process of producing with high yield a nitrocellulose product of low solution viscosity from cellulose fiber in shredded condition, that practice which comprises first treating the cellulose fiber in interfelted sheet form with a reagent that effects a marked lowering of the solution viscosity of the cellulose and shortens the fiber units while leaving them in the sheet, shredding the sheet to produce shredded stock of high bulkiness containing substantially all the short and fine fibers developed by the initial viscosity-lowering treatment, and nitrating the shredded stock containing such short and fine fibers to produce with high yield a nitrocellulose product of low solution viscosity.

2. In a process of producing with high yield a nitrocellulose product of low solution viscosity from cellulose fiber in shredded condition, that practice which comprises first treating the cellulose fiber in interfelted sheet form with an aqueous solution of a reagent that effects a marked lowering of the solution viscosity of the cellulose and shortens the fiber units while leaving them in the sheet, washing and drying the treated sheet, shredding the dried sheet to produce shredded stock of high bulkiness containing substantially all the short and fine fibers developed by the initial viscosity-lowering treatment, and nitrating the shredded stock containing such short and fine fibers to produce with high yield a nitrocellulose product of low solution viscosity.

3. In a process of producing with high yield a

nitrocellulose product of low solution viscosity from cellulose fiber in shredded condition, that practice which comprises first treating the cellulose fiber in interfelted sheet form with a dilute aqueous solution of mineral acid that effects a marked lowering of the solution viscosity of the cellulose and shortens the fiber units while leaving them in the sheet, drying the treated sheet, shredding the dried sheet to produce shredded stock of high bulkiness containing substantially all the short and fine fibers developed by the initial viscosity-lowering treatment, and nitrating the shredded stock containing such short and fine fibers to produce with high yield a nitrocellulose product of low solution viscosity.

4. In a process of producing with high yield a nitrocellulose product of low solution viscosity from cellulose fiber in shredded condition, that practice which comprises first treating the cellulose fiber in interfelted sheet form with an aqueous solution of oxidant that effects a marked lowering of the solution viscosity of the cellulose and shortens the fiber units while leaving them in the sheet, washing and drying the treated sheet, shredding the dried sheet to produce shredded stock of high bulkiness containing substantially all the short and fine fibers developed by the initial viscosity-lowering treatment, and nitrating the shredded stock containing such short and fine fibers to produce with high yield a nitrocellulose product of low solution viscosity.

5. In a process of producing with high yield a nitrocellulose product of low solution viscosity from cellulose fiber in shredded condition, that practice which comprises first treating the cellulose fiber in interfelted sheet form with the fumes of a mineral acid that effects a marked lowering of the solution viscosity of the cellulose, shredding the sheet to produce shredded stock of high bulkiness containing substantially all the fibers subjected to the initial treatment, and nitrating the resulting shredded stock to produce with high yield a nitrocellulose product of low solution viscosity.

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