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PAPER FOR NITRATION

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This invention relates to paper such as is intended for use as raw material in making cellulose esters and more especially nitrocellulose.

In accordance with the present invention, properly cooked and bleached hardwood sulphite pulps are used in the form of waterleaf papers for making nitrocellulose. Although such hardwood sulphite pulps have heretofore been ignored for nitration, I have determined that while such pulps give poor nitrocellulose yields and display very high acid retention when nitrated in shredded form, probably by reason of their short fiber length, they can be nitrated in the form of paper into high grade nitrocelluloses with high yield and low acid retention. These latter results are evidently a reflection of the excellent formation or substantially uniform texture realized in hardwood sulphite pulp papers even when the pulp is used in practically unbeaten condition, as hereinafter described, and the readiness and substantial uniformity with which they are penetrated by the nitrating acids.

I shall now give typical procedures for producing bleached hardwood sulphite pulps such as enter into the waterleaf papers hereof.

Example I.—Wood chips prepared as ordinarily from birch, beech, maple, or other hardwood are placed in a digester together with sodium base acid sulphite cooking liquor containing 1% combined SO_2 and 5% free SO_2. As used herein, the expression "free SO_2" means such sulphur dioxide as is available for neutralization by alkali. The digester contents are cooked by gradually heating them so as to reach 285° F. in six hours and maintaining such temperature for four hours and the digester pressure at 75 pounds gauge as a maximum, sulphur dioxide and steam being released at the end stages of cooking, if necessary. The hardwood sulphite pulp resulting from such cooking operation is thoroughly washed and then treated as a 4% stock suspension with 3% chlorine, based on the weight of dry pulp, for one hour at 140° F. The chlorinated stock is then washed and treated as an 8% stock suspension with a bleach liquor containing 6% sodium hypochlorite and 1.5% caustic soda, based on the dry weight of pulp, for six hours at 90° F. The resulting bleached pulp upon being washed and tested shows the following characteristics:

Alpha cellulose content	per cent	88
Viscosity (cuprammonium)	poise	0.5
Ether-soluble constituents	per cent	0.3
Lignin content	do	0.2

Example II.—The raw pulp is prepared as in Example I and is bleached in three steps. The first step involves treating the pulp as a 4% stock suspension with 4% sodium hypochlorite, based on the dry weight of pulp, for one hour at 70° F. The pulp is then washed and treated as an 8% stock suspension with 3% caustic soda, based on the dry weight of pulp, for four hours at 150° F. The pulp is then washed and treated as an 8% stock suspension with 5% sodium hypochlorite and 0.5% caustic soda, based on the dry weight of pulp, for four hours at 30° C. The resulting white pulp upon being washed and tested shows the following characteristics:

Alpha cellulose content	per cent	90
Viscosity (cuprammonium)	poise	1
Ether-soluble constituents	per cent	0.3
Lignin content	do	0.25

Example III.—This example is carried out like Example II, excepting that 1% red oil, based on the dry weight of pulp, is added to the caustic soda solution with which the pulp is treated in between the sodium hypochlorite treatments. The finished pulp corresponds substantially to that of Example II excepting that its content of ether-soluble constituents is reduced to 0.18% by reason of the emulsifying action of the sodium oleate formed from the red oil on the resinous or pitchy content of the pulp.

If desired, the sulphite cooking operation may be modified. Thus, the cooking liquor for the hardwood chips may be one containing 0.5% combined SO_2 and 5% free SO_2, in which case the cook is preferably performed so that the charge is gradually brought to a temperature of 275° F. in six hours and is maintained thereat for four hours with a maximum pressure of 75 pounds gauge. Such cooking conduces to a finished or bleached product of lower viscosity. Thus, when the resulting sulphite pulp is washed and put through the after-treatments of Example II, the bleached or finished product has the following characteristics:

	Per cent
Alpha cellulose content	89
Viscosity (cuprammonium)	0.5
Ether-soluble constituents	
Lignin content	0.1

In the foregoing examples, sodium base chemicals are specified because they promote the production of a finished pulp of especially low resin, lignin, and ash content. It is, however, possible to use other than sodium base chemicals, for instance, calcium base cooking liquor and/or calcium base bleach liquor.

Any one of the pulp products hereinbefore described may be formed into waterleaf papers admirably adapted for conversion into nitrocellulose. To this end, the pulp is preferably only lightly beaten, if at all, and run off on a papermaking machine so as to form waterleaf paper for nitration having a basis weight preferably less than about 60 pounds and a compactness value of at least about 60. These values bespeak a paper thickness not exceeding 0.01 inch, as can be seen from the definitions presently given. The expression "basis weight" as used herein means the weight in pounds of 480 sheets whose dimensions are 24 x 36''; and the compactness as given herein is determined by dividing the basis weight of the sheet in pounds by its thickness in inches and multiplying by the factor 10^{-2}. A typical waterleaf paper sheet answering the purposes hereof has a basis weight of 40 pounds and a compactness of 70; and such a paper hence has a thickness of .0057 inch.

In producing the waterleaf paper hereof, a cylinder or Fourdrinier papermaking machine may be employed and the press rolls at the wet end of the machine are suitably controlled or adjusted so as to yield a finished paper sheet of the desired compactness from the substantially unbeaten or lightly beaten pulp used as raw material. In some instances, it may be desirable to calender the resulting dry paper sheet, particularly as high compactness may be developed by calendering the dry sheet without unduly sacrificing the desired ready penetrability of the sheet by nitrating acid.

The hardwood sulphite pulp papers hereof may be nitrated in various forms, for instance, as small pieces or ribbons or as large sheets. Nitration may be performed with the usual mixed nitrating acids to produce nitrocelluloses of 11% to 12% or other nitrogen contents. Whereas, on the one hand, shredded hardwood sulphite pulp when nitrated to a nitrogen content of 12% with the usual mixed nitrating acid gives nitrocellulose yields of only about 140% and displays an acid retention of about 3, on the other hand, similar hardwood sulphite pulp in the form of the waterleaf paper hereof when similarly nitrated to a nitrogen content of 12% is attended by nitrocellulose yields of about 160% and acid retentions of about 1.4. These latter results are quite acceptable in the nitrocellulose industry. It is thus seen that the present invention makes available for the nitration industry sulphite pulps derived from a variety of hardwoods, e. g. birch, beech, maple, ash, oak, chestnut, poplar, etc., which, although occurring in abundance in various localities, have not heretofore been exploited as a source of cellulose for nitrocellulose manufacture.

The solution usually employed as a standard for measuring the viscosity of cellulose pulp is a cuprammonium cellulose solution of prescribed cellulose concentration, the viscosity being determined by measuring the time of efflux of a definite volume of such solution under standard conditions through an orifice of standard size. The solution viscosity of fiber as hereinbefore given in absolute C. G. S. units or poises is determined by measuring the viscosity of a solution of 6 grams of fiber in a cuprammonium solution composed of 225 cc. of 28.6% ammonia water containing 9 grams of so-called "copper hydrate" powder which is in reality basic copper nitrate corresponding in composition to the formula $Cu(NO_3)_2.3Cu(OH)_2$. The C. G. S. unit is employed because it is definite, denoting a viscosity 100 times that of water at 20° C., wherefore, a cuprammonium cellulose solution of standard composition identifying a fiber as having a solution viscosity of 10 is 1000 times as viscous as water at 20° C. The method of determining or measuring solution viscosity of cellulose fiber used herein is that described by me in much greater detail in "Industrial and Engineering Chemistry", volume 23, page 136, 1931; and inasmuch as the description of my viscosity-testing method as given in that publication affords the particular criterion or test used herein, it is to be understood that my reference to such description is intended to incorporate such description as a part hereof.

I claim:

1. A waterleaf nitration paper comprising substantially unbeaten, bleached, sulphite hardwood pulp having an alpha cellulose content not greater than about 90% and ether-soluble constituents amounting to not more than 0.3%, said paper being uniformly textured and readily penetrated throughout by nitrating acid and having a compactness of at least 60 and a thickness not exceeding 0.01 inch.

2. A waterleaf nitration paper comprising substantially unbeaten, bleached, sulphite hardwood pulp having an alpha cellulose content not greater than about 90%, ether-soluble constituents amounting to less than 0.3%, and a viscosity less than one poise, said paper being uniformly textured and readily penetrated throughout by nitrating acid and having a compactness of at least 60 and a thickness not exceeding 0.01 inch.

3. A method which involves making a waterleaf paper from cellulose pulp comprising substantially unbeaten, bleached, hardwood sulphite pulp having an alpha cellulose content not greater than about 90% and ether-soluble constituents amounting to not more than 0.3%, said papermaking operation being controlled to yield paper characterized by its uniform texture and ready penetratability by nitrating acid and having a compactness of at least 60 and a thickness not exceeding 0.01 inch, and nitrating the resulting paper.

4. A method which involves making a waterleaf paper from cellulose pulp comprising substantially unbeaten, bleached, hardwood sulphite pulp having an alpha cellulose content not greater than about 90%, ether-soluble constituents amounting to less than 0.3%, and a viscosity less than one poise, said papermaking operation being controlled to yield paper characterized by its uniform texture and ready penetratability by nitrating acid and having a compactness of at least 60 and a thickness not exceeding 0.01 inch, and nitrating the resulting paper.

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