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PROCESS OF MAKING ALPHA CELLULOSE

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This invention relates generally to the produc-
tion of high grade cellulose, and particularly to
the production of alpha cellulose of uniform
quality, and any desired viscosity.

Objects of the invention are: to obtain high
yields of alpha cellulose of high viscosity from
wood in general, and from hard woods in par-
ticular; to obtain a uniform product; to operate
in such manner that the viscosity can be con-
trolled; to provide an open vessel process so that
the process can be observed and controlled, and
so tests can frequently be made; to provide a
process by which a white pulp can be obtained
without substantial reduction in the degree of
viscosity, compared to other processes known to
us; to use waste acid from a previous run mixed
with fresh dilute nitric acid, the waste acid act-
ing as a catalyst to initiate and further reactions,
leading to uniform pulping action and uniform
yield and quality of alpha cellulose. This last
mentioned action is believed to be due to the
presence of nitrites in the waste liquor and serves
to initiate our dilute acid process.

The main object of this invention is to pro-
duce alpha cellulose of uniform, and any desired
viscosity from wood. An additional object is to
produce such a product by treatment of hard
wood, particularly aspen.

Another object is to produce alpha cellulose
which approximately is 98% pure; to produce
cellulose of high viscosity from hard woods or
short fiber woods; and to operate with a single
or multiple stage process to obtain the high
quality product mentioned above.

The following practicable examples are given
for purposes of illustration and, although each is
claimed, there is no intention to limit the broader
aspects of our invention to one of these examples.

Example I

To obtain alpha cellulose of high viscosity pro-
ceed as follows: Steep the wood, reduced to suit-
able size, such as sawdust, excelsior, or chips, for
example in 3% nitric acid, using the dilute acid
in an amount approximately six times the weight
of the wood, or in such proportion as to obtain
the proper volume relation of wood to liquor. The
wood should be held below the surface of the
liquid, and evaporation losses should be made up
by addition of water during steeping. Circula-
tion of the steeping liquor is desirable. Continue
this steeping for about 30 hours at about 70° C.
Then steam the chips for forty-five minutes, after
draining. The condensate is saved and re-used,

when the multiple stage process is practiced.
Then rinse the steamed chips (preferably with
hot as well as cold water) and cook at atmos-
pheric pressure for about two hours in 2% sodium
hydroxide. At this stage mild mechanical treat-
ment, such as heating, yields good pulp which
may be washed in the usual way. The crude pulp
obtained as above contains about 91-93% alpha
cellulose, has about 0.2-0.25% ash, has a 10%
KOH solubility of about 10-13%, and a copper
number of about 1.0. The cuprammonium vis-
cosity is high. The degree of viscosity obtained
at this stage very much more nearly approaches
the degree of viscosity obtained in cotton, and in
our experience is very much higher than ever has
been obtained at this stage by any pulping process
known to us. The viscosity as obtained by the
practice of this invention ranges from about 25
to 40 poises. The crude pulp made from aspen
wood is easy-bleaching and has high viscosity,
and is a feature of this invention.

To produce a high grade alpha cellulose, give
the pulp a preliminary bleach with chlorine using
an amount approximately 0.6% to 0.75% of the
weight of the air-dried pulp as chlorine, prefer-
ably adding the bleach in two or three portions
over a period of about one hour. Then treat the
pulp with nine to ten times its dry weight of 6%
sodium hydroxide at ordinary temperatures for
ten to twenty minutes. As a final bleach, treat
the pulp with sodium hypochlorite in an amount
approximately 0.15% of the dry weight of the
pulp for two hours. The final product contains
about 98% alpha cellulose, about 0.1% or less ash,
has a 10% KOH solubility of about 3½% to 6%
and a copper number of about 0.5. The vis-
cosity is high, ranging from 10 to 13.6 poises,
when determined by the falling-ball method in a
solution of the following composition: 20 grams
of cellulose per liter; 30 grams of copper per
liter; 165 grams of ammonia (NH₃) per liter;
10 grams of sugar per liter.

A method for the determining of the cupram-
monium viscosity is as follows: The cuprammo-
nium solution is first prepared using for example,
about 31.1 grams of copper, 171.3 grams of NH₃
and 10 grams of sugar, per liter. The solution
is made by pouring concentrated NH₃ solution
over copper turnings and then bubbling air up-
wardly therethrough, the container being main-
tained at 10-20° C. The correct concentration is
then obtained by adding ammonia water. Am-
monia is titrated directly with 2 normal H₂SO₄
and methyl red indicator. The copper is deter-
mined by the Law modification of the De Haen's

iodide method. Before final adjustment of concentration the cuprammonium solution is allowed to stand for several days. It is then decanted and filtered to remove as much suspended copper or copper oxide as possible. The correct concentration is then obtained by adding ammonia water. Ammonia is titrated.

In testing, the pulp is air dried at 40° C. A moisture determination is made. 1.96 bone dry grams of air dried material are weighed and placed in a dissolving bulb. 4 cc. of distilled water is added. The bulb is then tightly stoppered and allowed to stand for three hours. The bulb is then attached to the charging apparatus and opened at each end. N₂ is blown through at about 2 mm. Hg pressure for 60 seconds. By means of a three-way cock, the bulb is alternately evacuated and filled with N₂, three times. The bulb is then left under a vacuum, connected with a pipette, and 97 cc. of cuprammonium solution is added. N₂ is added to bring the pressure up to atmospheric. The dissolving bulb is tightly closed with screw clamps and the rubber stoppers wired on and sealed with beeswax. Then kept in an ice box at 50° F. for 12 hours. Then agitated 24 hours at 25° C., removed and placed in a thermostat at 30° for 1½ hours. The bulb is then shaken by hand to insure homogeneity. It is then attached to a ring stand. The upper end is attached to a source of N₂ and about 15 to 20 cc. of solution is purged from the lower end. The lower end is then connected by a short rubber tube (closed with a pinch clamp) to the viscosity tube. The whole is then transferred to the thermostat. The tube is set vertically by means of a plumb. The solution is then forced into the viscosity tube. A strong light source is placed back of the viscosity tube, and after five minutes, fine 3 mm. glass balls are dropped through the solution, one after the other. The time required to fall between two marks 15 cm. apart, is measured with a stop watch.

The degree of viscosity will vary somewhat in accordance with slight changes in operating conditions, and with the exact details of bleaching, but will be uniform for any particular method. By uniformity of product, we mean that the products from different batches or runs made under the same operating conditions will have the same characteristics of viscosity, 10% KOH solubility and copper number, that is the same characteristics as given by any commonly used laboratory criteria. The ability to get uniformity is closely related to operation in an open vessel.

Example II

To produce alpha cellulose of medium viscosity, proceed as above with the following modifications: Steep the material with 3½% nitric acid in approximately the same ratio of wood to liquor as in Example I, for about thirty hours at about 75° C. Steam and cook as in Example I. For preliminary bleaching, use chlorine equal to about 1¼% of the weight of the air dried pulp, operating as in Example I. Apply caustic treatment as above with 6-8% NaOH. For the final bleaching, use sodium hypochlorite equal to about 0.2% of the dry weight of the pulp, operating for about two hours. This viscosity is medium and ranges from 4.6 to 5.9 poises, which is somewhat higher than the best commercial alpha cellulose made from wood.

Example III

To produce a pulp of low viscosity the following modifications are necessary: Steep with 4½% nitric acid for about thirty hours at 80° C. Steam and cook as Example I. For preliminary bleaching, use chlorine equal to about 2% of the weight of air dried pulp operating as in Example I. Treat as in Example I with 8% to 10% NaOH. For the final bleach, use sodium hypochlorite in an amount equal to about 0.3% of the dry weight of the pulp for about two hours.

An important feature of this invention is to add to the raw steep liquor about 2% to 5% by volume of waste acid from a previous run, and this applies to all three of the preceding examples.

It occasionally happens that with a low concentration of acid even at a relatively high temperature, the reaction (clearly detectable by change in color and odor) may not start. We have found that the addition of a small amount of waste acid from a previous run initiates the chemical reaction. In other words, we have discovered that we can catalyze the reaction by the use of a small amount of waste acid from a previous run. We believe that this catalytic action is due to nitrites in the waste liquor. This insures uniformity and insofar as we know is a new discovery. Uniformity is more important than any other one thing, and we obtain uniformity in all the characteristics and particularly in viscosity.

A unique feature is the mildness of the cooking obtainable, for example, by cooking in an open vessel, so that the process can be observed and controlled at all times. This does not preclude the use of vacuum or low pressure, or any other suitable operation for obtaining a mild cook. We have also found that uniformity cannot be obtained as readily with a high concentration acid process, as with a low concentration acid process.

The following is given as an example of our multiple stage process:

Example IV

In this case the use of 4% nitric acid gives excellent results by steeping the comminuted wood for about thirty hours at about 60° C.; with three or four stages. In a four-step steep, the acid is used as follows: For steep I, drainings from steep II of a previous run are combined with steam condensate from a previous run. For steep II, drainings from steep III of a previous run are used. For steep III, drainings from steep IV of a previous run are used, and for steep IV, fresh acid is used. In each case, the total acidity (with phenolphthalein) of the used acids, expressed as HNO₃, is brought up to 4% by the addition of fresh HNO₃. If the total volume of acid is too low, this is brought up to the desired value. Steep II to IV require only about five-sixths of the amount of dilute acid needed for steep I. The drainings from steep I are discarded, or may be treated for recovery of nitric acid, oxalic acid, or acetic acid.

Example V

Another procedure is as follows: A mixture of NaNO₃ and H₂SO₄ is used as a less expensive source of nitric acid. For this method, the conditions of steeping must be changed. For a single step steep, the steeping liquor may be as follows: H₂SO₄ equivalent to 5% HNO₃, and NaNO₃ 75 equivalent to 4% to 4½% HNO₃. The tempera-

ture of operation is about 80° C. and the time is about thirty hours.

Example VI

In a multiple stage steep the same steeping procedure is followed as for HNO₃ when used alone. The temperature of operation is about 80° C. and the time is about thirty hours. H₂SO₄ equivalent to 5% HNO₃, and NaNO₃ equivalent to 3½% to 4% HNO₃.

After any of the above mentioned steeping procedures, the drained chips or wood in other suitable form, are steamed directly for from one-half to one-hour, the condensate being saved and re-used as indicated, if steeping is multiple-stage. The wood is then rinsed, preferably with hot as well as cold water and the mass is cooked in about 2% NaOH, or chemical equivalent, for about two hours at atmospheric pressure. Mechanical treatment then yields a good pulp which may be washed in the usual way.

The pulp may be given a preliminary bleach with chlorine, or its equivalent, using about 1% of the weight of the pulp as chlorine. The pulp is washed and may be treated with 6-10% NaOH with the pump at about 9% to 10% stock concentration, at ordinary temperatures, for ten to fifteen minutes, after which it is washed and given a final bleach using 0.1% to 0.2% of the weight of the pulp.

In any of the above procedures, woodchips of the size ordinarily used in any pulp mill can be used, or wood in any other suitable form or size may be used. Vacuum impregnation of the wood with a steeping acid has been recommended but at the steeping temperatures given above, no special impregnation treatment is necessary, and this is a feature of our invention.

We have discovered that the use of 10% to 15% HNO₃ has the following disadvantages: Such high concentrations are far too expensive, since it does not seem possible to continuously recycle the used HNO₃. The product has a low viscosity, and the 10% KOH solubilities of the purified pulps are much higher than the desired value.

A very valuable feature and modification of our invention relates to the use of excelsior. We have found that there are distinct advantages in using excelsior. The time necessary for the operation is reduced, the temperatures can be increased without detrimental results, and the nitric acid concentration can be reduced with equally good results. For example, the temperature may range from 75° to 95° C. and the time may be 6 to 24 hours, depending, of course, on the temperature and concentration of the acid used. Nitric acid concentrations of 1½% to 3½% may be used and the amount of such dilute acid may be from seven to nine times the weight of the wood. The steam treatment is about one-half to one hour for either excelsior or for chips. Sawdust or wood in any other suitable form would require slight modification in the cooking conditions, but could be used.

By our process, the total yield of crude pulp is in the neighborhood of 45% of the weight of the chips, and this has about a 91-93% quality. The present process gives a high yield of high quality pulp and insofar as we know, no one but ourselves has ever before produced a crude pulp which runs 91-93% alpha cellulose.

Pulp made by our process requires less bleaching than the ordinary pulp. If too much bleach is used in the final step, the viscosity, as well

as the 10% KOH solubility are quite unfavorably affected. Our process enables us to use a very small quantity of hypochlorite (or equivalent bleach) for the final bleaching, the range being approximately from 0.1 to 0.25% of hypochlorite. By the use of our process, both bleaching operations require less bleaching material. Of course, if it is not desired to increase the percentage of alpha cellulose, in the pulp, a pulp product of good whiteness containing 92% to 94% of alpha cellulose can be obtained by eliminating the caustic soda treatment and simply neutralizing, washing, and going on with the bleaching.

It must be again emphasized that operation at atmospheric pressure in an open vessel gives a control of the process leading to a product having uniform properties, which is a factor of utmost importance. Insofar as we are aware, no one has even before discovered a process in which the degree of viscosity can be unfailingly controlled. In all cases, we use less than 5% concentration of nitric which is a big saving in acid. In all commercial processes known to us, high or low pressures and high temperatures are used, necessitating the use of closed vessels so that the operator cannot be sure of what is going on. Moreover, it was previously thought impossible to produce alpha cellulose of high viscosity from short fibered wood, but we have discovered that this is not true, and disclose herein a process by which such material can be produced from such wood.

With chips, a very good specific nitric acid concentration is about 3% for a high viscosity pulp. The amount of nitric acid being equal to about 18.7% of the weight of the air-dried chips. For excelsior, the best specific dilutions are about 1½% of nitric acid, the time about 18 hours and the temperature about 85°, the amount of nitric being about 13.9% of the weight of the air dried wood.

It is, of course, understood that any suitable source of nitric acid may be used, such for example as nitric acid produced by the oxidation of ammonia or by treating a salt of nitric acid with sulphuric acid.

Note that a white pulp can be obtained without severe bleaching, and about 98% alpha cellulose pulp can be produced. It is of course understood that bleaching does not affect the percentage of alpha cellulose but affects the degree of viscosity.

The following factors as steps in the process are, among other factors and steps, claimed in various combinations: Nitric acid concentration ranging up to 5%; the proportion of acid to wood ranging from 6 to 9 times the weight of the wood; the time ranging from 6 to 30 hours, dependent on the state of division of the wood; the temperature ranging from 60° to 95° C., the steaming treatment time ranging from ½ to 1 hour; the amount of the preliminary bleach with chlorine (or equivalent) ranging from 0.6% to 2% of the weight of the air dried pulp; the NaOH or equivalent treatment ranging from 5% to 10% and the amount of final bleach ranging from 0.15% to .3% of the dry weight of the pulp.

To recapitulate some of the features and advantages of the invention: Less nitric acid is used; severe bleaching is avoided; the process may be carried out in an open vessel under atmospheric pressure; relatively low operating temperatures are used; high viscosity alpha cellulose pulp can be produced from short fibered

(hard) woods; the discovery that there is no particular connection between the length of the fibers and of viscosity; the ability to control the degree of viscosity; the ability to start the process when using very dilute acid, and to obtain proper softening, by adding to the nitric acid or to the batch a part of the waste acids (solvents and solutes) from a previous run; the ability to extract oxalic acid in relatively larger quantities than usual. The discovery of a way to obtain high viscosity alpha cellulose from aspen wood or bass wood and other woods; the use of aspen wood or other wood excelsior; the discovery of the modifying effect of wood, in the form of excelsior, on the process in allowing reduction of the operating time, and allowing use of higher temperatures.

We claim as our invention:

1. Process for the manufacture of cellulose from wood, which comprises first treating the wood with an aqueous nitric acid of a concentration between 2 and 10% at a temperature below 95° C., and then subjecting the so-treated wood to a two stage treatment with an alkali, the first stage being a treatment with a hot weak alkali solution and the second stage being a treatment with a cold strong alkali solution.

2. A process for producing alpha cellulose from hardwood which comprises, initially steeping said hardwood for about six hours or more in an aqueous solution consisting substantially of from about 1½% to less than 5% HNO₃ maintained at a temperature of from about 60° C. to about 85° C., and thereafter cooking the steeped product with a dilute caustic alkali solution.

3. A process for the manufacture of alpha cellulose pulp from hardwood which comprises, initially steeping said hardwood with an aqueous solution consisting substantially of 3% HNO₃ for about 30 hours maintained at a temperature of about 70° C., thereafter cooking the steeped product with a dilute caustic alkali solution, and then bleaching said product.

4. A process for the manufacture of alpha cellulose pulp from aspen wood which comprises initially steeping said aspen wood with an aqueous solution consisting substantially of 3% HNO₃ for about 30 hours maintained at a temperature of about 70° C., thereafter cooking the steeped product with a dilute caustic alkali solution, and then bleaching said product.

5. A process for producing alpha cellulose of uniform viscosity from hardwood which includes initially steeping said hardwood for about six hours or more in an aqueous solution consisting of from about 1½% to less than 5% HNO₃ maintained at a temperature of from about 60° C. to about 85° C., cooking the steeped product with a dilute caustic alkali solution, then preliminarily lightly bleaching with chlorine, thereafter treating the pulp with from about 6% to 10% solution of caustic alkali and lightly bleaching said pulp with a bleaching agent.

6. A process for producing alpha cellulose of uniform viscosity from hardwood which includes initially steeping said hardwood for about six hours or more in an aqueous solution consisting of from about 1½% to less than 5% HNO₃ maintained at a temperature of from about 60° C. to about 85° C., cooking the steeped product with a dilute caustic alkali solution, then preliminarily lightly bleaching with chlorine, thereafter treating the pulp with a solution of caustic alkali and then lightly bleaching said pulp.

7. A process for producing alpha cellulose of uniform viscosity from hardwood which includes initially steeping said hardwood for about six hours or more in an aqueous solution consisting of from about 1½% to less than 5% HNO₃ maintained at a temperature of from about 60° C. to about 85° C., cooking the steeped product with a dilute caustic alkali solution, then preliminarily lightly bleaching with chlorine, thereafter treating the pulp with a solution of from about 6% to 10% sodium hydroxide and lightly bleaching said pulp with sodium hypochlorite.

8. The method for producing alpha cellulose of high quality from aspen wood which comprises, initially steeping said aspen wood for about six hours or more in an aqueous solution consisting substantially of from about 1½% to less than 5% HNO₃ maintained at a temperature of from about 60° C. to about 85° C., steaming the steeped material, rinsing the material, thereafter cooking the steeped product with a dilute caustic alkali solution, then preliminarily lightly bleaching with chlorine, then treating with from about 6% to 10% sodium hydroxide solution at room temperature and finally lightly bleaching said material with sodium hypochlorite.

9. A process for producing alpha cellulose of uniform viscosity from hardwood which comprises, initially steeping said hardwood for about six hours or more in an aqueous solution consisting substantially of from about 1½% to less than 5% HNO₃ maintained at a temperature of from about 60° C. to about 85° C. in the presence of a small volume of waste solution from a previous similar treatment, and thereafter cooking the steeped product with a dilute caustic alkali solution.

10. A process for producing alpha cellulose from hardwood which comprises, initially steeping said hardwood for about six hours or more in an aqueous solution consisting substantially of from about 1½% to less than 5% HNO₃ maintained at a temperature of from about 60° C. to about 85° C. at atmospheric pressure, and thereafter cooking the steeped product with a dilute caustic alkali solution.

11. A process for producing alpha cellulose from aspen wood which comprises, initially steeping said aspen wood for about six hours or more in an aqueous solution consisting substantially of from about 1½% to less than 5% HNO₃ maintained at a temperature of from about 60° C. to about 85° C. at atmospheric pressure in an open vessel, and thereafter cooking the steeped product with a dilute caustic alkali solution.

12. A process for producing alpha cellulose from hardwood which comprises, initially steeping said hardwood for about six hours or more in from about 6 to about 9 times the weight of the wood in an aqueous solution consisting substantially of from about 1% to less than 5% HNO₃ maintained at a temperature of from 60° C. to 85° C., and thereafter cooking the steeped product with a dilute caustic alkali solution.

13. A method for producing alpha cellulose of high quality and uniform viscosity which consists in treating wood with nitric acid of about 3% strength for about thirty hours at about 70° C., then steaming the treated material for about forty-five minutes, rinsing and adding 2% sodium hydroxide and cooking for about two hours, then preliminarily bleaching by use of chlorine in an amount equal to about 0.6% to 0.75% of the weight of the air dried pulp, adding the chlorine in two or three portions over a period

of about an hour, then treating the pulp with about nine to ten times its dry weight of 6% sodium hydroxide for ten to twenty minutes at room temperature and finally bleaching for approximately two hours by using sodium hypochlorite amounting to approximately 0.15% of the dry weight of the pulp.

14. A method for producing alpha cellulose of high quality and uniform viscosity which consists in treating comminuted hard wood with nitric acid of 5% or less strength for from about twenty-four to thirty hours at from 60° to 80° C., then steaming the treated material for about forty-five minutes, rinsing and adding 2% sodium hydroxide and cooking for about two hours, then preliminarily bleaching by use of chlorine in an amount ranging from about 0.6% to 2% of the weight of the air dried pulp, then treating the pulp with about nine to ten times its dry weight of 6% to 10% sodium hydroxide for ten to twenty minutes at room temperature and finally bleaching for approximately two hours by using sodium hypochlorite ranging from about 0.15% to 0.3% of the dry weight of the pulp.

15. A method for producing alpha cellulose of high quality and uniform viscosity which consists, in steeping properly comminuted raw wood with nitric acid of less than 5% strength for about 30 hours at from about 60 to 85° C., then steaming the treated material, rinsing the ma-

terial, then adding dilute sodium hydroxide and cooking at atmospheric pressure, then preliminarily bleaching by the use of chlorine in an amount equal to about .06 to 2% of the weight of the air dried pulp, then treating the pulp with about nine to ten times its dry weight of 6 to 10% sodium hydroxide, and finally bleaching using sodium hypochlorite amounting to approximately 0.15 to 0.3% of the dry weight of the pulp.

16. A method for producing alpha cellulose of high quality and uniform viscosity which consists, in steeping properly comminuted wood in an open vessel with nitric acid ranging from about 1½ to 4½% strength in an amount about six to nine times the weight of the wood for about 30 hours at from about 65 to 85° C., then steaming the treated material, rinsing the material with water, then cooking at atmospheric pressure for about two hours in 2% sodium hydroxide, then preliminarily bleaching by the use of chlorine in an amount equal to about 0.6 to 2% of the weight of the air dried pulp for about an hour, then treating with about six to ten times its dry weight of 6 to 10% sodium hydroxide for 10 to 20 minutes at room temperature, and finally bleaching for approximately two hours using sodium hypochlorite amounting to approximately 0.15 to 0.3% of the dry weight of the pulp.

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CERTIFICATE OF CORRECTION.

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It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 3, first column, line 25, for "pump" read --pulp--; page 4, first column, line 70, claim 6, for "60%" read --60°--; and second column, line 61, claim 12, for "1%" read -- $1\frac{1}{2}\%$ --; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 12th day of January, A. D. 1943.

(Seal)

Henry Van Arsdale,
Acting Commissioner of Patents.