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PROCESS OF DIGESTING CELLULOSIC AND LIGNEOUS MATERIALS.

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The present invention relates to the preparation of paper pulp, and is based upon my discovery that even very dilute solutions of certain salts can be used as the cooking liquor, with the production of very satisfactory results.

The particular sulfates which I have found to be most suitable in the present invention are the sulfates of metals having atomic weights between 23 and 39.1, namely sodium sulfate, magnesium sulfate, and potassium sulfate, either alone or mixed with other sulfates or salts especially the sulfates of aluminum, chromium, manganese, iron, nickel, cobalt, copper and zinc. Other salts can also be added if desired, particularly the salts of the alkali metals and the soluble salts of the akaline earth metals.

After extensive research, I have found that the above substances are highly useful for the production of the cooking liquors.

In my copending application 616,609, filed February 2, 1923 (which case is largely a continuation of matter from an earlier Case Ser. No. 407,759, filed Sept. 2, 1920), I have described the use of sulfates and mixtures of sulfates including those above referred to, and particularly including sulfates of the metals having atomic weights between 23 and 39.1, in the form of mixtures of these sulfates with each other, or mixtures of one or more of these sulfates with other substances. In the said prior application, I recommended the use of solutions containing about 2 to 5% of the sulfates in question, and I have now found that for the production of the better grades of paper, resembling kraft paper, solutions of a very much lower concentration can be used, especially solutions containing between about 0.05 and 0.2% (figured as anhydrous salts), these highly diluted solutions giving even better results than the stronger solutions referred to in the said prior application.

The process is applicable not only to coniferous woods, but various other woods, including hard woods, and other plant growth such as straw, sedges, bamboo and cane and the like. The process has given very satisfactory results with coniferous woods including spruce, hemlock, balsam and the pines, and these woods will hereinafter be more completely discussed, but it is to be understood that the process is of broad application, with respect to the cellulosic and ligneous materials under treatment.

I give the following examples, but it is to be understood that the examples are given purely for the purpose of illustration, and not of limiting the invention thereto.

Example 1.

A digestive solution is made up containing 1¼ ounces of a mixture of equal parts of crystallized sodium sulfate and crystallized magnesium sulfate, to each five gallons of the liquor. This would correspond to about 0.2% of the crystallized salts, or about 0.1% of the anhydrous salts, (it will be noted that these crystallized salts both contain large proportions of water of crystallization amounting in this instance to somewhat over 50% of the weight of the crystallized salts).

The spruce wood, from which the pulp was to be prepared, was first split, with an axe into pieces about two feet long and three quarters of an inch to two inches square. The prepared material accordingly would not ordinarily be referred to as "chips", but it more nearly resembled furnace kindling wood in size. In other words, spruce billets, 2 feet long as they come to a paper mill, are simply flitch-split into boards and while in the machine splitter are again split at right angles to the first splits, into kindling if desired.

I particularly call attention to the fact that in splitting the wood in this manner, there is no conversion of the wood into sawdust, and the pieces of wood, when so prepared, are free from sawdust and wood flour. Substantially the whole of the wood becomes thereby readily convertible into long-fibered pulp, whereas in other methods including the ordinary chipping processes, a substantially greater part of the individual fibres are cut or broken. The pieces of wood were then packed into a cage, and placed into a digester and were covered with the solution. In this particular case some of the wood was partially dry, some with 10%, 30% and 50% moisture, and a heavy iron perforated plate was placed on top of the cage containing the wood to keep the latter from floating. Sufficient of the liquor was used to completely submerge the pieces of wood, and to fill the digester to within about two inches of the top. The cover of the digester was then put on and bolted into place and the digester contents were then heated by gas flames at the bot-

tom of the digester, until the temperature in the digester had risen to about 212° F. The fires were then shut out and the digester and its contents were allowed to stand over night, during which time the liquor of course cooled off and the pieces of wood became throughly impregnated with the cooking liquor.

The following morning the fires were again started, and the digester heated up, all while still closed, until a pressure of about 80 pounds existed in the digester, as shown by the steam gage located on the cover of the digester. The temperature at this stage was about 300° F., and the gas flames were then turned down so as to maintain this condition for about two and one half hours, after which the gas flames were extinguished and the digester allowed to cool until the pressure had dropped to about atmospheric. The digester was then opened and the cage of wood taken out, and the cage with its contents placed in a tank of water and allowed to stand therein for a short time, say 45 minutes.

Some of the pieces of wood were then mashed by being lightly hammered on a hard surface, and the material was then run through a shredder to reduce the same to a coarse pulp and was then introduced into a beating engine, the beater roll having been raised about 25 turns from the said plate, and the brushing of the material was started. At intervals of half an hour, more or less, the beater roll was lowered one or two turns at a time, and the brushing operation continued for about four or five hours, at the end of which time it was found that the cooked material had been reduced to a pulp of uniform consistency and some of this pulp was then sheeted with the production of a very high grade paper resembling kraft paper in appearance and of a strength better than ordinary kraft paper.

In this example I did not wash out at any stage of the process, any of the inter-cellular materials nor did I use screens of any kind except for sheeting the product, the product amounting to about 90% of the dry weight of the wood treated. The product was virtually "plastic wood" free of shives and dirt, with the full contents of the wood except the water solubles.

Example 2.

In this example balsam wood is employed, the digestive solution being composed of sodium sulfate and magnesium sulfate, in approximately molecular proportions, namely about one half ounce of crystallized magnesium sulfate ($MgSO_47H_2O$) and about three quarters of an ounce of crystallized sodium sulfate ($Na_2SO_410H_2O$) per five gallons of water.

The operation was conducted as above described and the finished product was about as good as that above described, both as to strength and appearance.

Experiment 3.

Green pine wood, prepared in the same manner as the spruce wood in Example 1, was cooked in a liquor containing 1½ ounces per 5 gallons of a mixture of sodium sulfate, magnesium sulfate and aluminum sulfate (all crystallized salts averaging about 50% of water) these three salts being in the proportions approximately of their molecular weight. The details of this operation were substantially the same as in Example 1, and a very high grade pulp was produced.

I call attention to the fact that in the process of this invention, the wood or other plant growth can be in a green or dry or wet state, as desired, and it is advisable in all cases to thoroughly impregnate the wood, before raising the temperature to much above 212° F., with the digestive solution, this can be accomplished by pressure, preferably while the temperature is not substantially above 212° F., and in some cases the pressure can be preceded by a vacuum treatment in the digester.

Any size of pieces of wood can be used, which can be penetrated by the liquor.

I call attention to the fact that in this process, the pieces of wood do not cook up into the form of a pulp during the process, but retain substantially their original size and shape throughout the cooking operation.

The cooked pieces can be passed lengthwise through suitable pressure rolls, to mash the same without breaking the individual fibers, and the material can then be passed through a shredder or a pulper, or the sticks can be reduced direct into a beater or first crushed in any suitable device, for example an edge runner, without breaking the individual fibers.

The beating operation should preferably be a brushing one, conducted slowly and at the beginning of the operation the roll of the beater should be raised a considerable distance above the bed plate, in order to "tease out" the separate fibers, without breaking the fibers.

While the cooking operation does not reduce the woody material to a pulp, the cementitious matter in the wood is rendered friable so that it can be crushed, without substantially injuring the fibers. The use of large material of this kind in the digestive operation makes it advisable to remove the cooked material from the digester without blowing, and for this purpose I have found that the use of metal cages made of wire mesh material is advisable. For large scale operations rotary digesters can be used or stationary upright digesters with bottom

arranged for dumping into a pit or upon a concrete floor, or into cars. The cooking operation does not dissolve or destroy the lignin in the wood, and I believe that it does not dissolve anything out of the wood except the water soluble matter, while rendering the cementitious matter readily friable by a blow and a jet of water. The wood is rendered soft.

As examples of particular mixtures of salts to be employed, in addition to the above, I mention sodium sulfate and ferrous sulfate, sodium sulfate, magnesium sulfate and sea-salt or sodium nitrate, mixtures of sodium sulfate and kainite. The quantities of these various salts can be adjusted more or less, but I prefer to employ quantities between about 0.05% and about 0.2% (figured as anhydrous salts) for the total concentration.

It will be understood that I do not employ caustic alkalies, sulfids or mineral acids (e. g. SO_2) in combination with the above.

The term "cooking" is herein used to designate the portion of the treatment during which a temperature substantially above 212° F., is maintained in the digester. The term "digesting" is of broader significance in that it includes any and all portions of the treatment of the cellulosic and ligneous material during which the said material is in contact with the solution, and the latter is heated to above atmospheric temperature, whether said temperature is above 212° F., or not. The term "soaking" is employed to designate contact of any liquid with said material, whether at or above atmospheric temperature and pressure.

My researches indicate that various other salts can be used as the sole (or at least the principal) ingredients of the digestive solution, in about the proportions above indicated, examples of such salts being iron sulfate, copper sulfate, zinc sulfate, kainite, sea salt, sodium nitrate, these salts being used alone or in the form of mixtures, in total concentration substantially below 1% and preferably 0.05 to 0.5%. Sea water diluted to this strength can also be used.

In the above experiments, the air initially in the top of the digester was not blown off during the heating up of the solution, so that the pressure was slightly higher than would normally correspond to the temperature employed or stated otherwise the temperature was somewhat lower than would correspond to the pressures employed.

In practice of the process, I find that it is convenient to employ an unlined iron digester, which of course makes the process cheaper and in a digester of a given size, the non-use of a thick brick lining leaves room in the digester for more material and correspondingly more of the digestive solution. It appears to be advisable to employ iron (or steel) in contact with the cooking liquor, as better results seem thereby to be produced, perhaps on account of the catalytic action of iron. There seems to be no considerable chemical action of the digestive solution on the iron.

For heating the liquor in the digester, and also for cooling the same, the steam and the cool water respectively can be passed through a coil located in said digester, no claim for that feature being made herein.

In practice of the process the solutions can be used at least four times, (small additions of new chemicals being made from time to time, if desired).

The use of sodium sulfate and magnesium sulfate above referred to has given especially favorable results. These can be referred to as "sulfate of an alkali-forming metal," since the hydroxids and oxids of both these metals act as alkalies.

I claim:—

1. A process of preparing cellulosic and ligneous materials for pulping which comprises cooking the same in a solution of an alkali-forming metal sulfate, of substantially below 1% strength, which solution is substantially free from caustic alkalies, soluble sulfides and sulfurous acid, until the cementitious matter in said cellulosic and ligneous material, while retaining its initial physical structure, is rendered readily friable by pressure, without thereby reducing such material to a pulp.

2. A process of preparing cellulosic and ligneous materials for pulping which comprises cooking the same in a solution of a metal sulfate of substantially below 1% strength, which solution is substantially free from caustic alkalies, soluble sulfides and sulfurous acid, under superatmospheric pressure of about 75 to 85 lbs. per square inch, until the cementitious matter in said cellulosic and ligneous material is rendered readily friable by pressure, whereby the cellulosic and ligneous material retains its initial structure, without thereby reducing such material to a pulp.

3. A process of preparing cellulosic and ligneous materials for pulping which comprises cooking the same in a solution of an alkali-forming metal sulfate of about 0.05 to 0.2% strength, figured as anhydrous salts, until the cementitious matter in said cellulosic and ligneous material, while retaining its initial physical structure, is rendered readily friable by presure, without thereby reducing such material to a pulp.

4. A process which comprises cooking cellulosic and ligneous material in an aqueous liquor containing an alkali-forming metal sulfate as its principal active dissolved constituent and which liquor is substantially free from caustic alkalies, soluble sulfides

and sulfur dioxide, the strength of such solution being about 0.05 to 0.2%, figured as anhydrous salts.

5. A process which comprises cooking cellulosic and ligneous material under a superatmospheric pressure of about 70 to 85 lbs. and at a temperature of from 275 to 350° F., maintained for from 1 to 4 hours, in an aqueous liquor containing a soluble sulfate as its principal active dissolved constituent, the strength of such solution being about 0.05 to 0.2%, figured as anhydrous salts.

6. A process which comprises cooking cellulosic and ligneous material in an aqueous liquor containing a mixture of an alkali metal sulfate and another sulfate, together in amount equal to about 0.05 to 0.2%, figured as anhydrous salts, as its principal active dissolved constituents, such liquor being substantially free from caustic alkalies and sulfurous acid.

7. A process which comprises cooking cellulosic and ligneous material in an aqueous liquor containing a mixture of an alkali metal sulfate and an earth metal sulfate, together in amount equal to about 0.05 to 0.2%, figured as anhydrous salts, as its principal active dissolved constituents.

8. A process which comprises cooking cellulosic and ligneous material in an aqueous liquor containing a mixture of an alkali metal sulfate and magnesium sulfate, together equal to about 0.05 to 0.2%, figured as anhydrous salts, as its principal active dissolved constituent, such liquor being substantially free of sulfids, free alkalies and free mineral acids.

9. A process which comprises cooking cellulosic and ligneous material in an aqueous liquor containing a mixture of an alkali metal sulfate and magnesium sulfate, together equal to about 0.1% figured as anhydrous salts, as its principal active dissolved constituent.

10. A process which comprises cooking cellulosic and ligneous material in an aqueous liquor containing a plurality of sulfates, as its principal active dissolved constituents, such sulfates being present in amounts substantially in proportion to their molecular weights, the concentration of said solution being a minor fraction of 1% and such liquor being substantially free from sulfurous acid.

11. A process which comprises cooking cellulosic and ligneous material in an aqueous liquor containing a mixture of an alkali metal salt and another salt, which salts do not react upon each other to form insoluble compounds, and which salts form the principal dissolved active constituents of the said liquor, the strength of such solution being about 0.05% to 0.2%, figured as anhydrous salts.

In testimony whereof I affix my signature.

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