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EXTRACTION OF CELLULOSE FROM VEGETABLE MATTER

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This invention relates to the extraction of cellulose from vegetable matter containing ligno-cellulose by acid or neutral liquors of mineral salt type and constitutes an improvement over known processes.

It is known that during the delignification of vegetable matter containing ligno-cellulose by cooking with mineral salts such as neutral sulfite or by bisulphite liquors the fibres become colored of which the intensity and hue depend on the raw materials employed and the process of digestion adopted. In most cases the fibres must undergo subsequent treatments for clarification or bleaching.

It is an object of the invention to produce pulp by these processes that is of better color and which requires no after treatment.

Another object is to improve the cooking liquors of this type. Another object is to stabilize the improved liquors with novel stabilizers. Yet another object is to improve the homogeneity of the pulps produced by these processes. Another object is to eliminate or minimize the occurrence of black spots in such pulps.

The objects of the invention, generally speaking, are accomplished by digesting the vegetable matter containing ligno cellulose in a neutral or acid liquor containing at least one of the sulphites ind bisulphites of alkali and alkali earth metals, which are used in the usual concentrations, and a metal hydrosulphite, preferably zinc or sodium hydrosulfite, the liquor preferably being stabilized, especially when the temperature of the cook is to be about 120–170° C., by the addition of stabilizers of which formaldehyde, complex chelates, and polyphosphates are exemplary. I have also discovered that ethylenediaminetetracetic acid is an exceptionally efficient stabilizer.

By this invention one produces directly, by digesting cellulosic vegetable matter with mineral salts, pulps which are both less colored and more homogeneous than was previously feasible. The hydrosulfites of sodium and zinc are particularly useful. The amount to use depends on the kind of ligno-cellulosic matter being digested and the conditions, such as temperature, of the cook. In general good results are obtained if one uses a proportion of hydrosulfite on the order of .3% to 2% of the weight of the dry cellulose matter. At the same time one uses of the non-alkaline sulfite or bisulfite the same proportions that are presently recommended.

The cooks that are carried out under pressure employ temperatures that are relatively high, circa 120° to 170° C., at which the hydrosulfites are relatively unstable, and under such circumstances it is desirable to add a stabilizer for the hydrosulfite to the liquor. Satisfactory stability is obtained with stabilizers of the type of formaldehyde, complex chelates, ethylene diamine tetraacetic acid, polyphosphates.

In carrying out the cook in the presence of hydrosulfite the formation of a part of the colored products is prevented. The hydrosulfites have marked reducing

power and prevent the oxidation of the sugars and other organic products released in the disintegration of the vegetable materials, or destroy them after formation, thus producing a clearer and less colored pulp. In addition, at the relatively high temperature of such cooks the hydrosulfites, because of their combined sulfur, which occurs in different forms, plays the double role of a delignifying agent and assists in the production of more homogeneous and softer pulps. By decomposition during digestion the hydrosulfite gives, according to the pH of the cooking liquor, the following reactions:

With a neutral liquor, sodium hydrosulfide:

$$3Na_2S_2O_4+3H_2O=5NaHSO_3+NaHS$$

With a sulfurous acid medium, hydrogen sulfide:

$$3Na_2S_2O_4+SO_2+4H_2O=6NaHSO_2+H_2S$$

The products NaHS and H_2S are delignifiers of strength and their action is added to that of the cooking liquors of alkali metal, or alkali, sulfite or bisulfite base and produce jointly a disintegration of the vegetable matter that is more thorough and more homogeneous. From this fact, the presence of sodium hydrosulfite in the cooking liquor makes the action of the mineral salt liquors more selective and protects the cellulose better.

The invention is applicable to all the liquors employing mineral salts in acid or neutral medium and to all types of vegetable matter from pine wood to straw. This produces clearer pulps which may be used directly without bleaching, particularly if the medium is the neutral sulfite or bisulfite with hydrosulfite.

Among the useful hydrosulfites are the alkali and alkali earth metal hydrosulfites and zinc hydrosulfite. Sodium hydrosulfite is excellent and is generally employed, but it is not exclusively useful.

The pulps produced by this method can be bleached by the standard methods. Particularly interesting results are obtained by submitting such pulps to a simple treatment with sodium hydrosulfite under conditions the same as those used for bleaching groundwood pulp. The improvement in whiteness is greater than that obtained with pulps not made in the presence of hydrosulfite.

In all cases the process produces pulp that is better cooked and more homogeneous than by prior art methods, making bleaching easier. An advantage of technological and commercial nature arises from the fact that the chemicals and steam used in the digesters may be reduced while producing a pulp at least equal to that previously obtainable. No modification of present standard apparatus is necessary.

The following examples are exemplary, not limiting.

Example 1

The cooking of 2.5 kg. of poplar wood chips, 89% dry, by a mixture of calcium and magnesium sulfite in water at standard concentration, was carried out in a pressure digester (autoclave) of stainless steel. The cooking liquor, at the time of admission to the digester, containing its necessary water, had the following composition:

	G./l.
SO_2, total	60
CaO	7.7
MgO	3.3

105° was reached in 3 hrs. 45 min. When the pressure had reached 100 kg., the temperature was maintained for 5 hrs., then in 1 hr. 15 min. the temperature was raised to 128° and maintained there for 6 hrs., so that the whole cook required 16 hrs. The digester was then opened, discharged, and the product was washed and sent to the beaters. The pulp was studied. Standard

test samples gave 52% reflectance with a Wratten blue filter. The pulp contained some nodules and numerous black spots.

Operating under identical conditions, but with the addition of 1.8% sodium hydrosulfite stabilized by .2% ethylene diamine tetraacetic acid the pulp was free of nodules and contained only a few black spots. The standard samples had a reflectance of 60% by the same filter.

Bleaching with sodium hydrosulfite (1% on the weight of the dry fibres) at 35° for 30 minutes produced another gain in whiteness of 11 points, the final reflectance 71%.

Example 2

2.5 kilos of Landes pine chips, 70–75% dry, were cooked in a liquor containing a mixture of bisulfites of calcium and magnesium in an autoclave of stainless steel. The liquor at the start of the operation, mixed with the chips contained:

	G./l.
SO_2, total	60
CaO	7.7
MgO	3.3

A temperature of 105° C. was reached at 3 hrs. and 45 min. When the pressure reached 5 kg. it was maintained for 5 hrs. When the temperature reached 128°, which required 1 hr. 15 min. from 105°, a second steady cook of 6 hrs. was used, so that the total cook was 16 hrs.

The digester was blown, the product was washed and sent to a disintegrator. The pulp was examined, standard test samples showed reflectance of 45% with a Wratten blue filter and revealed lumps and numerous black spots.

Operating under the same conditions, but with the addition of 2% of sodium hydrosulfite stabilized by .6% formaldehyde there was obtained a pulp free from lumps and with very few black spots. The same test showed a reflectance of 51%, an improvement of 6 points.

Example 3

A pulp was prepared from 2.5 kg. of poplar wood chips, 89% dry, using neutral sodium sulfite liquor buffered with sodium carbonate of which the composition, by weight based on the dry wood, was:

	Percent
Sodium sulfate	14
Sodium carbonate	4.5

The same conditions as Example 1 were used except that the steady cook took place at 160° for 7 hrs. The pulp had a reflectance, by like test, of 51%.

When the operation was repeated but with the addition of 1% sodium hydrosulfite, stabilized by .3% formaldehyde, the reflectance of a standard sample was 56%, a gain of 5 points.

This pulp could be used directly for making printing paper without bleaching.

Comparable results are obtainable using other hydrosulfites, particularly zinc hydrosulfites.

As many apparently widely different embodiments of the present invention may be made without departing from the spirit and scope thereof, it is to be understood that the invention is not limited to the specific embodiments.

What is claimed is:

1. In the extraction of cellulose from vegetable matter containing ligno-cellulose by mineral salts in neutral and acid media, the improvement which comprises digesting the vegetable matter in a liquor containing at least one of the sulfites and bisulfites of alkali and alkali earth metals, a metal hydrosulfite, of a metal from the group Zn and Na, in an amount between about .3 to about 2% by weight of the dry ligno-cellulose matter, and a stabilizer for the hydrosulfite, consisting in its essential operative constituent of ethylene diamine tetraacetic acid, at a temperature of 120–170° C.

2. In the extraction of cellulose from vegetable matter containing ligno cellulose by mineral salts in neutral and acid media, the improvement which comprises digesting the vegetable matter in a liquor containing at least one of the sulfites and bisulfites of alkali and alkali earth metals, a metal hydrosulfite, in an amount between about .3 to about 2% by weight of the dry lignocellulose matter, and as a stabilizer for the hydrosulfite, ethylene diamine tetraacetic acid, at a temperature of 120–170° C.

3. In the extraction of cellulose from vegetable matter containing ligno cellulose by mineral salts in neutral and acid media, the improvement which comprises digesting the vegetable matter in a liquor containing at least one of the sulfites and bisulfites of alkali and alkali earth metals, a metal hydrosulfite, in an amount between about .3 to about 2% by weight of the dry ligno cellulose matter, and a stabilizer for the hydrosulfite, at a temperature of 120–170° C.

4. In the extraction of cellulose from vegetable matter containing ligno-cellulose by mineral salts in neutral and acid media, the improvement which comprises digesting the vegetable matter in a liquor containing at least one of the sulfites and bisulfites of alkali and alkali earth metals, a metal hydrosulfite, in an amount between about .3 to 2% by weight of the dry ligno-cellulose matter, and ethylene diamine tetraacetic acid.

5. In the extraction of cellulose from vegetable matter containing ligno-cellulose by mineral salts in neutral and acid media, the improvement which comprises digesting the vegetable matter in a liquor containing at least one of the sulfites and bisulfites of alkali and alkali earth metals, a metal hydrosulfite, and a stabilizer for the hydrosulfite.

6. In the extraction of cellulose from vegetable matter containing ligno-cellulose by mineral salts in neutral and acid media, the improvement which comprises digesting the vegetable matter in a liquor containing at least one of the sulfites and bisulfites of alkali and alkali earth metals, a metal hydrosulfite from the group consisting of alkali metals and zinc, and ethylene diamine tetraacetic acid.

7. A cooking liquor of non-alkaline pH composed in its essential delignifying ingredients of at least one of the sulfites and bisulfites of alkali and alkali earth metals, a metal hydrosulfite, and a hydrosulfite stabilizer.

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