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MANUFACTURE OF CELLULOSE

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Our present invention relates to the manufacture of cellulose and, more particularly, contemplates an improvement in the manufacture of cellulose by alkaline digestion.

One of its objects is a process of obtaining an improved cellulose by conducting the chlorinating treatment which follows the alkaline digestion in a manner as will be described hereafter. Another object is the improved cellulose obtainable by our new process. Further objects will be seen from the detailed specification following hereafter.

It is known that hard sulfite pulps or sulfate pulps, more particularly so-called kraft pulps, are preferably subjected to a preliminary treatment with chlorine whereupon the chlorination products are removed by treatment with a weakly alkaline solution in order to promote their degree of digestion and thereby render them more accessible to the subsequent bleaching operation.

Careful studies have proven that the pulps, more particularly sulfate pulps, digested in an alkaline medium, suffer a reduction of their viscosity already when subjected to the aforesaid chlorinating treatment and, therefore, a loss of solidity. The reason for this behavior of the pulp lies in the fact that the reaction between the chlorine which is necessary in rather large quantities for the chlorination of such strongly incrustated pulps and the ligneous matter occurs but comparatively slowly, so that, when conducting the chlorination under normal conditions, the bath which becomes acid in the treatment will contain an excessive amount of free chlorine for a prolonged period of time, to which the cellulose obtained by an alkaline digestion process is very sensitive. Furthermore, working in open vessels, such as hollanders, is much impeded in that the workmen are inconvenienced by the development of odors.

The process proceeds in such a manner that the chlorine which first enters into reaction is rapidly absorbed by the ligneous substance contained in the outer layers of the fibers, water-soluble and alkali-soluble products being formed. In the same proportion as the chlorination proceeds to the inner layers the chlorination of the water-insoluble incrusts which have already been attacked by the chlorine, becomes more difficult. The chlorine is more and more prevented from reacting with the inner incrustated layers, so that the bath gradually is enriched with chlorine. The consequence of this is a reduction of the viscosity and tensile strength of the cellulose.

This drawback may be overcome by causing the

chlorine to react at such a slow rate that it is continuously and completely absorbed by the incrusts of the cellulose pulp, so that the incrusts are practically chlorinated in a bath which is free from chlorine. But because in this case the chlorine, especially during the addition of the last third of the required amount, is consumed only very slowly, the duration of the chlorination would have to be prolonged too long from the commercial point of view.

According to this invention the time of chlorination may be considerably reduced without damaging the fibers by taking care that in the same proportion as the chlorine is brought into reaction, the chlorination products formed are dissolved by the addition of an exactly dosed amount of alkali such that the pH-value of the bath is maintained between 6 and 9, preferably between 7.5 and 8.5.

It has already been proposed to react on cellulose pulp first with alkali and then with chlorine gas or to react on cellulose pulps with alkali and chlorine simultaneously. In both cases, however, the amount of alkali present was so large that hypochlorite was formed. Therefore, the conditions of reaction of these known processes were completely different from those of a chlorination according to this invention and, as experiments have proven, by the known processes, the cellulose pulp suffered a strong reduction of viscosity and the resistance was greatly injured. In contradistinction thereto, according to this invention, the formation of hypochlorite is avoided by controlling the addition of the alkali, so to dissolve the added quantity is just sufficient that the chlorinated ligneous substances which are soluble in an alkaline solution. When proceeding in this way, the amount of chlorine which may be brought into reaction in a shorter period of time, is greater than that used for an ordinary chlorination in an acid medium.

This fact can be explained from what has been set forth above. By maintaining a pH-value of about 8 the chlorinated ligneous substances which are soluble in alkali are dissolved off and the following layers are now readily accessible to the action of the chlorine. The digestion, therefore, takes place in a more uniform, a more intense, and a more rapid manner. In consequence, the bath will not become enriched with chlorine, and the cellulose is not attacked. By these means not only an improvement of the Sieber number is obtained while the viscosity remains unchanged, but the treatment conducted under such mild conditions yields a cellulose of

an increased resistance also against chemical influences in the finishing of the pulp. The new process also involves the advantage that it completely avoids foaming caused by the formation of carbonic acid which is abundantly produced particularly in the treatment of kraft pulps rich in ligneous substances. The new process can be carried out in any receptacle which guarantees a thorough and rapid mixture of the pulp with the chemical agents, the density of the pulp depending on the capacity of the mixing tank. By avoiding the formation of larger quantities of free chlorine in the bath, it also becomes possible to work in open vessels, without inconvenience by odors. Moreover, by keeping the reaction of the bath in a more or less neutral state, any wear of the armatures, washing drums, and so on is avoided.

The experiments set forth in the following table have been carried out in such a manner that the bath, after finishing the chlorination step, was alkaline so as to correspond with an 0.05 per cent. caustic soda solution. After this treatment the pulp was washed. The advantages presented by the process according to this invention may be seen from the following table:

	Start- ing mate- rial	Acid me- dium		New pro- cess	
Quantity in per cent. of chlo- rine, calculated on absolutely dry pulp.....		5	5	5	6
Duration of chlorination in minutes.....		103	390	105	240
Copper viscosity.....	837	655	746	728	693
Sieber number.....	50	17.9	18.66	18.3	8.9

Since by the continuous addition of alkali the main quantity of the chlorinated incrusts is dissolved already during the chlorination process, another noteworthy economy of chlorine may be realized by taking care that the dissolved chlorinated products are removed by simultaneously adding water and removing the treating liquid, as may be effected, for instance, by lowering the washing drum into the hollander, because the products already chlorinated absorb a further amount of chlorine besides the amount of chlorine necessary for their dissolution in alkali. This observation has been verified by an experiment carried out while simultaneously washing with water under which conditions with the application of only 4 per cent. of chlorine, a cellulose was produced having a copper viscosity of 791 and a Sieber number of 13.

Because with sulfate pulp only a small part of the chlorination products are soluble in water, the continuous washing with water, as has likewise been established by experiments, when carried out according to the method hitherto in practice, that is without a continuous addition of alkali, could not lead to an improvement.

A further improvement of the process according to this invention may be obtained by performing the chlorination in at least two steps with the intercalation of a wash with a solution of alkali whereby the chlorine brought into reaction in the first step may amount to 60 to 80 per cent. of the quantity of chlorine required. Since in the first chlorination, according to our observations, the cellulose is not injured, this step may, if required, be carried out in the usual manner. It is only in the second step that the chlorination must be conducted according to

the new process, i. e. simultaneously neutralizing the bath. This is clearly demonstrated by the following two comparative experiments.

	Chlorina- tion acid in both steps	First step: acid, second step: pH 7.5 to 8.0
Amount in chlorine in percent of chlorine.....	3.7+1.0	3.7+1.4
Duration in minutes of the chlorination.....	70+180	70+60
Copper viscosity.....	628	736
Sieber number.....	11.2	9

This mode of operation also involves a considerable reduction of the cost for alkali.

As a matter of fact the second step can be carried out with continuous washing with water.

The following example illustrates the invention:

1000 kilos of kraft pulp having a Sieber number of 60 are chlorinated with 3.7 per cent. of chlorine in the form of chlorine water in a hollander provided with a washing drum. To avoid any excess of chlorine in the bath, the chlorination lasts about 2 hours. Then the pulp is thickened, washed, and mixed with such an amount of alkali that the bath contains about 0.05 per cent. of NaOH. After the alkali has reacted half an hour, the content of the hollander is thoroughly washed. This treatment is followed by a second chlorination with 1.1 per cent. of chlorine while simultaneously adding alkali. The chlorine water is run in, for instance, at a substantial distance before the bucket or the propeller of the hollander near the bottom. The alkali required, which may be any soluble alkali, used alone or in mixture, however preferably caustic soda, is added in a highly dilute condition at a substantial distance behind the mixing device where the chlorine is practically consumed. During the whole chlorination process the bath must be maintained at a pH-value of 6.5 to 9.0. The quantity of NaOH necessary for this effect amounts to about 1.3 per cent., calculated on the quantity of the pulp. This chlorination step likewise lasts about 2 hours, and its duration depends on the intensity of the mixing device or the speed of propulsion of the hollander. When the chlorination is complete the fiber pulp is mixed with so much alkali that its content of NaOH amounts to 0.05 per cent. and after half and hour's reaction the pulp is thoroughly washed. The cellulose thus obtained has a viscosity of 740 which is practically its original viscosity but the Sieber number has been reduced to about 8.

The advantages involved in the method described reside among others in the high quality of the unbleached material, inasmuch as the resistibility of its fibers complies with the highest requirements. At the same time the pulp has a lower Sieber number than any known, commercial, highly bleachable sulfite pulp or sulfate pulp. Due to its light yellow color, the flexibility of its fibers and their excellent resistibility, its freedom from resin and its low content of incrusts, it is well suited for the preparation of special papers of any kind.

Due to its low content of ligneous substance such a pulp may be transformed, without strongly impairing its viscosity and the resistibility of the fibers by oxidizing agents such as the chloride of lime or sodium hypochlorite, when employed in the usual concentration, into a product which can be bleached perfectly white. It is clear that the higher the viscosity of the starting material the more intense may be the bleaching operation for

the production of a highly white material. This, also, is one of the special advantages obtained by the new cautious yet vigorous chlorination. The bleaching operation is preferably carried out as it is described in U. S. Patent 1,801,876, i. e. while maintaining the reaction slightly alkaline in the bleaching operation by the addition of a small quantity of a caustic alkali, a hydroxide of the alkaline earths including magnesium hydroxide.

The bleaching is conducted preferably at a temperature above 40° C., for instance, between 40° C. and 80° C.

All the advantages presented by the present invention come out, however, much more distinctly, if an unbleached sulfate pulp, after chlorinating the same in the manner described, to dissolve out its hemi-cellulose and increase its contents of alpha-cellulose, is first subjected to an alkaline refinement and then to a bleaching operation. Thus there can be obtained highly viscous improved celluloses which not only are suitable for the preparation of special papers, but can also be employed for chemical processes, for instance the manufacture of artificial silk, such as viscose silk or cellulose acetate silk. The process, furthermore, involves the advantage that such refined cellulose, the viscosity of which has been greatly spared, can be transformed into products of a lower viscosity which are exceptionally white, by subjecting it to a suitable and vigorous bleaching.

The values of viscosity given in the specification have been ascertained by measuring the time of outflow of a copper oxide ammonia solution containing 1 per cent. of cellulose. The copper oxide ammonia solution employed is adjusted to contain exactly 20 per cent. of NH_3 and 1.3 per cent. of copper; the manipulations are performed in an atmosphere of nitrogen for the exclusion of oxygen. The values are calculated under consideration of the water value of the viscosimeter.

What we claim is:

1. A process of manufacturing cellulose which comprises treating a cellulose pulp obtained by alkaline digestion with chlorine while maintaining during the chlorination a pH-value between 6 and 9 by continuous addition of alkali.

2. A process of manufacturing cellulose which comprises treating a cellulose pulp obtained by alkaline digestion with chlorine while maintaining during the chlorination a pH-value between 6 and 9 by continuous addition of alkali, removing part of the treating liquid, and adding a quantity of water equal to the quantity of treating liquid removed.

3. A process of manufacturing cellulose which comprises treating in a first step a cellulose pulp obtained by alkaline digestion with 60 to 80 per cent. of the chlorine to be employed in the chlorinating treatment, washing the pulp free from acid, treating the pulp in a second step with the further 20 to 40 per cent. of chlorine while maintaining a pH-value between 6 and 9 by continuous addition of alkali.

4. A process of manufacturing cellulose which comprises treating in a first step a cellulose pulp obtained by alkaline digestion with 60 to 80 per cent. of the chlorine to be employed in the chlorinating treatment, washing the pulp free from acid, treating the pulp in a second step with the further 20 to 40 per cent. of chlorine while maintaining a pH-value between 6 and 9 by continuous addition of alkali, adding to the pulp so much alkali that its concentration amounts to at least 0.05 per cent., and washing the pulp with water.

5. A process of manufacturing cellulose which

comprises treating a cellulose pulp obtained by alkaline digestion with chlorine while maintaining during the chlorination a pH-value between 6 and 9 by continuous addition of alkali, removing part of the treating liquid, and adding a quantity of water equal to the quantity of treating liquid removed, adding to the pulp so much alkali that its concentration amounts to at least 0.05 per cent., and washing the pulp with water.

6. A process of manufacturing cellulose which comprises treating in a first step a cellulose pulp obtained by alkaline digestion with 60 to 80 per cent. of the chlorine to be employed in the chlorinating treatment, washing the pulp free from acid, treating the pulp in a second step with the further 20 to 40 per cent. of chlorine while maintaining a pH-value between 6 and 9 by continuous addition of alkali, adding to the pulp so much alkali that its concentration amounts to at least 0.05 per cent., washing the pulp with water, and bleaching the pulp while maintaining the pulp slightly alkaline.

7. A process of manufacturing cellulose which comprises treating in a first step a cellulose pulp obtained by alkaline digestion with 60 to 80 per cent. of the chlorine to be employed in the chlorinating treatment, washing the pulp free from acid, treating the pulp in a second step with the further 20 to 40 per cent. of chlorine while maintaining a pH-value between 6 and 9 by continuous addition of alkali, adding to the pulp so much alkali that its concentration amounts to at least 0.05 per cent., washing the pulp with water, and bleaching the pulp at a temperature of 40 to 80° C. while maintaining the pulp slightly alkaline.

8. A process of manufacturing cellulose which comprises treating in a first step a cellulose pulp obtained by alkaline digestion with 60 to 80 per cent. of the chlorine to be employed in the chlorinating treatment, washing the pulp free from acid, treating the pulp in a second step with the further 20 to 40 per cent. of chlorine while maintaining a pH-value between 6 and 9 by continuous addition of alkali, adding to the pulp so much alkali that its concentration amounts to at least 0.05 per cent., washing the pulp with water, treating the pulp with a solution of caustic alkali of 5 to 12 per cent. strength, and washing the pulp with water.

9. A process of manufacturing cellulose which comprises treating in a first step a cellulose pulp obtained by alkaline digestion with 60 to 80 per cent. of the chlorine to be employed in the chlorinating treatment, washing the pulp free from acid, treating the pulp in a second step with the further 20 to 40 per cent. of chlorine while maintaining a pH-value between 6 and 9 by continuous addition of alkali, adding to the pulp so much alkali that its concentration amounts to at least 0.05 per cent., washing the pulp with water, treating the pulp with a solution of caustic alkali of 5 to 12 per cent. strength, washing the pulp with water, and bleaching the pulp while maintaining the pulp slightly alkaline.

10. A process of manufacturing cellulose which comprises treating in a first step a cellulose pulp obtained by alkaline digestion with 60 to 80 per cent. of the chlorine to be employed in the chlorinating treatment, washing the pulp free from acid, treating the pulp in a second step with the further 20 to 40 per cent. of chlorine while maintaining a pH-value between 6 and 9 by continuous addition of alkali, adding to the pulp so much alkali that its concentration amounts to at least

0.05 per cent., washing the pulp with water, treating the pulp with a solution of caustic alkali of 5 to 12 per cent. strength, washing the pulp with water, and bleaching the pulp at a temperature of 40 to 80° C. while maintaining the pulp slightly alkaline.

11. A process of manufacturing cellulose which comprises treating a cellulose pulp obtained by alkaline digestion with chlorine while maintaining during the chlorination a pH-value between 6 and 9 by continuous addition of alkali, removing part of the treating liquid, and adding a quantity of water equal to the quantity of treating liquid removed, adding to the pulp so much alkali that its concentration amounts to at least 0.05 per cent., washing the pulp with water, treating the pulp with a solution of caustic alkali of 5 to 12 per cent. strength, and washing the pulp with water.

12. A process of manufacturing cellulose which comprises treating a cellulose pulp obtained by alkaline digestion with chlorine while maintaining during the chlorination a pH-value between 6 and 9 by continuous addition of alkali, removing part of the treating liquid, and adding a quantity of water equal to the quantity of treating liquid removed, adding to the pulp so much alkali

that its concentration amounts to at least 0.05 per cent., washing the pulp with water, treating the pulp with a solution of caustic alkali of 5 to 12 per cent. strength, washing the pulp with water, and bleaching the pulp while maintaining the pulp slightly alkaline.

13. A process of manufacturing cellulose which comprises treating a cellulose pulp obtained by alkaline digestion with chlorine while maintaining during the chlorination a pH-value between 6 and 9 by continuous addition of alkali, removing part of the treating liquid, and adding a quantity of water equal to the quantity of treating liquid removed, adding to the pulp so much alkali that its concentration amounts to at least 0.05 per cent., washing the pulp with water, treating the pulp with a solution of caustic alkali of 5 to 12 per cent. strength, washing the pulp with water, and bleaching the pulp at a temperature of 40 to 80° C. while maintaining the pulp slightly alkaline.

14. An unbleached cellulose pulp produced by alkaline digestion and to a great extent freed from impurities, said pulp having a viscosity of about 700 and a Sieber-number of about 10.

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