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MULTISTAGE CELLULOSE PULP BLEACHING WITH CHLORINE AND CHLORINE DIOXIDE

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ABSTRACT OF THE DISCLOSURE

Bleaching cellulose pulp in a multistage process wherein the pulp at low consistency (2.5–3.5%) is bleached with chlorine, then treated with alkali to remove the major portion of the lignon content of the pulp, and thereafter treated with an excess of elemental chlorine at a pulp concentration of not less than 5% and at a temperature of below 35° C. Small amounts of chlorine dioxide (0.5–2 gm./kilo of pulp) may optionally be added to the elemental chlorine in the second chlorine treatment step. Subsequent treatment stages may follow which include alkali washes and chlorine dioxide bleachings.

High requirements are placed on the purity of the products obtained when manufacturing bleached, chemical cellulose. A large majority of the impurities found in the finished product originates from bark or discoloured fibre bundles. The presence of discoloured fibre bundles may be due to the fact that owing to its denser structure a certain percentage of the wood was not sufficiently impregnated during the digestion process or because for some reason or other pulping in the digester was not effected uniformly. In addition to separating knots during the knot separating operation large pieces of portly delignified wood, which cannot be easily broken up, are also removed. Upon additional screening, which is also normally undertaken, further smaller fragments of wood (so-called shives) and possibly particles of bark are removed. The extent to which the pulp is freed from the aforementioned impurities depends on how well the screening operation is carried out. Naturally, the economic factor sets a limit to the extent to which the pulp can be subjected to purification by means of screening. It has also been shown in practice that a purified pulp which has been subjected to the most careful screening always contains a certain amount of shives of varying size, the colour of which may vary from c. golden brown to an almost black.

The principle intention when bleaching screened chemical pulp is to increase the brightness of the pulp by removing lignin and other substances. This is often effected by means of a sequence of bleaching stages, including treatments using, for instance, chlorine, hypochlorite, chlorine dioxide, peroxide, alkali etc. Removal of the lignin is most easily effected from discrete fibres, which are more freely accessible to the influence of the bleaching chemicals. However, lignin is, to a certain extent, also released from the, in part, strongly lignin-containing fibre bundles (shives), whereby these can either be disintegrated completely into discrete fibres or disintegrated into smaller fibre bundles. The colour of the shives may, at the same time, fade somewhat. The aforegoing concerning fibre bundles originating from the wood is also true for the particles of bark entrained with the pulp to the bleaching department.

It is apparent from the foregoing that in addition to expecting a brighter pulp from the bleaching process a cleaner pulp is also anticipated, i.e. a pulp with less impurities in the form of shives and bark than in the case of unbleached pulp. In view of the present high requirements placed on the purity of the bleached pulp the ability of the bleaching process to purify the pulp is of great importance. It can be mentioned in this context that in many cases as few as ten specks per square metre of sheet pulp may lead to such a depreciation in the quality of the pulp that the pulp must be sold at a reduced price.

One method commonly used in modern plants to further increase the purity of the bleached pulp is to treat the pulp in a cyclone purifier, but even after undergoing such a treatment troublesome amounts of impurities still remain in the pulp.

It has long been known to bleach cellulose pulp with chlorine or chlorine dioxide, either separately or in mixture. Chlorine bleaching of the unbleached pulp is usually effected at low temperatures (preferably below 20° C.) and with low consistency (2.5–3.5%) and short bleaching periods (30–90 minutes). The low pulp consistency is adopted for two reasons, firstly to obtain a rapid and uniform intermixing of the chlorine in the pulp suspension, which is necessary for obtaining a uniform chlorination of the pulp at the rapid reaction which takes place between the chlorine and lignin, and secondly to avoid sharp rises in temperature in the pulp suspension owing to the strong exothermic reaction between chlorine and lignin, since high temperatures lead to an uncontrollable oxidative decomposition of the pulp. Chlorine dioxide bleaching is effected at high temperatures (60–70° C.) and long bleaching periods (3–6 hours).

It is also known that an addition of a small amount of chlorine dioxide when using chlorine to bleach cellulose pulp can reduce the oxidative decomposition of the cellulose pulp.

With the development of thick-pulp pumps it has become possible to bleach at high pulp concentrations. This possibility has been utilized when bleaching with chlorine dioxide and hypochlorite and when treating the pulp with alkali but has not been applied when bleaching with chlorine, since bleaching with chlorine in the first bleaching stage, as mentioned above, involves a very rapid reaction between chlorine and lignin under strong generation of heat, which in the case of high pulp concentrations uncontrollably raises the temperature of the suspension, causing an oxidative decomposition of the pulp which is difficult to overcome and resulting in a reduction in the strength of the bleached pulp. Further, when treating unbleached pulp, the reaction speed between chlorine and lignin is so high that at high pulp concentrations difficulties are met with in achieving a uniform distribution of the bleaching agent, resulting in non-uniform chlorination of the pulp, which leads to an impaired bleaching result.

In order to obtain a bleached pulp possessing the highest possible degree of purity the bleaching conditions are intensified, e.g. by raising the temperature or increasing the amounts of bleaching agent added, in excess of that necessary for obtaining the required brightness of the pulp. This involves significant increases in the costs of the bleaching process.

By analyzing the effect of the bleaching process on shives and pieces of bark it has been possible to show that particles of a certain maximum size in the unbleached pulp are completely disintegrated and bleached during the normal bleaching process whilst particles of larger dimensions remain to a certain extent in the pulp. By intensifying the bleaching process, by increasing the chemical charge, the said maximum limit can be raised to include larger and larger particles; but this involves an increase in costs. The maximum permitted size of contaminating

wood and bark particles in the unbleached pulp varies firstly with the digesting process, which determines the bleachability of the particles, and secondly according to the degree of intensity with which the chosen bleaching process acts upon the said particles. As can be seen from the following Example 1 and Table 1 the maximum size of the particles can be determined from case to case by analyzing the percentage of shives in the pulp prior to the bleaching process and subsequent to the same.

EXAMPLE 1

2% shives of various thickness, calculated on the weight of the pulp, obtained by fractioning screened reject removed from the screening section of the sulphite plant, was added to a two-stage sodium-sulphite pulp digested, washed and screened in the plant. The pulp was then bleached in five stages (Cl_2, NaOH, ClO_2, NaOH, ClO_2), partly with normal charges of chlorine and partly at 76% excess chlorine in the first bleaching stage, but in other respects under the same bleaching conditions and the same chemical charge. The increase in specks in the finally bleached pulp, caused by the addition of shives, was determined, see tests 1–3 in Table 1. Corresponding tests were also made on a sulphite pulp which included shives taken from the screening department of the sulphate factory, and which had been digested, washed and screened in the plant, the bleaching process, however, being carried out in seven stages (Cl_2, NaOH, Cl_2, NaOH, ClO_2, NaOH, ClO_2) tests 4–6 in Table 1. The tests show how the number of specks are influenced by the thickness of the shives and the treatment with excess chlorine in the first bleaching stage.

TABLE 1

Test No.	Pulp mixture	Increase in number of specks per 100 g. bleached pulp caused by the addition of shives: Normal chlorination in stage 1	76% excess chlorine in stage 1
	Sulphite pulp plus 2% shives:		
1	0.35 mm. thick	0	0
2	0.35–0.50 mm. thick	317	97
3	0.50–0.80 mm. thick	1,550	547
	Sulphate pulp plus 2% shives:		
4	0.35 mm. thick	10	10
5	0.35–0.50 mm. thick	104	43
6	0.50–0.80 mm. thick	887	163

The object of the present invention is to provide a simple and economic process for increasing the purity of the pulp.

A substantially pure and also brighter pulp is obtained by means of a process according to the invention in that the pulp in a prebleached state and high concentration is subjected within a multistage bleaching operation to an excess of chlorine. The tests made have shown that subsequent to prebleaching the pulp, e.g. by chlorinating in diluted pulp suspension and subsequent alkali treatment

of the pulp, it is possible to treat the said pulp with an excess of chlorine at high pulp concentration without any detrimental increase in temperature of the pulp suspension, and thus no subsequent decomposition of the pulp. The tests have also shown that it is possible to effect a good and economic bleaching of the pulp and its shives if an excess of chlorine is introduced into the pulp suspension at mass concentrations which exceed 5%, suitably 10–13%, particularly if the chlorination process is carried out for long periods, e.g. 2–6 hours. In that the major portion of the lignin in the unbleached pulp has already been removed during the prebleaching process it is now possible, by means of a small amount of chlorine, to obtain a strong excess of chlorine in the pulp suspension, the majority of which chlorine exists during the entire bleaching period, thus meaning that not only the separated fibres havve obtained good penetration and bleaching but also the fibre bundles and particles of bark.

The temperatures at which the bleaching stage according to the invention is carried out need not be too high, suitably below 35° C., e.g. 20–30° C., in order to avoid oxidative decomposition of the pulp. For the same reason it is convenient to carry out the bleaching stage according to the invention in the presence of a small amount of ClO_2, suitably 0.5–2 gram/kilo of pulp, calculated as active chlorine. The advantages gained from this bleaching process are apparent from the following Examples 2 and 3.

EXAMPLE 2

A two-stage sodium-sulphite pulp digested, washed and screened in the factory and to which was added 0.5% shives, calculated on the weight of the pulp, having a thickness of 0.35–0.50 mm. and which were obtained by fractioning, in a slotted screen, screen rejects taken from the screening department of the sulphate plant, was bleached in five stages according to the bleaching sequence Cl_2, NaOH, Cl_2+ClO_2, NaOH, ClO_2 for various lengths of time and at various pulp concentrations in the third bleaching stage according to Table 2, but in other respects under the same bleaching conditions and chemical charge. The speck area obtained in the finally bleached pulp by the addition of shives was then determined. The brightness and viscosity of the pulp was also determined. The results are disclosed in Table 2. The table also shows a test where no addition of ClO_2 was made in the third bleaching stage.

TABLE 2

Bleaching sequence: Cl_2/NaOH/Cl_2+ClO_2/NaOH/ClO_2

Test No.	ClO_2 gram active, Cl/kilo pulp	Pulp conc., percent	Bleaching stage 3: Time, min.	Bleaching stage 3: Rest-chlorine, gram/kilo pulp	Finally bleached pulp: Brightness, percent SCAN	Finally bleached pulp: Viscosity, cp. Tappi	Finally bleached pulp: Speck area, mm.^{2}
8	2	3.5	60	17.2	93.0	97	37.2
9	2	3.5	180	17.4	93.0	84	10.4
10	2	10	60	9.15	93.6	89	5.0
11	2	10	180	7.92	94.5	82	2.7
12		10	180	7.67	94.0	37	3.8

EXAMPLE 3

0.5% shives were added to a pine wood sulphate pulp, digested, washed and screened in the factory, the shives were 0.5–0.7 mm. thick and were obtained by fractioning the reject from the screening department of the sulphate factory, in a slotted screen. The pulp was bleached in seven stages according to bleaching sequence Cl_2, NaOH, Cl_2+ClO_2, NaOH, ClO_2, NaOH, ClO_2 for various lengths of time and at different mass concentrations in the third bleaching stage according to Table 3, but in other respects

under the same bleaching conditions and chemical charges. The speck area obtained in the finally bleached pulp by the addition of shives was then determined. The brightness and viscosity was also determined, the result can be seen from Table 3.

TABLE 3

Bleaching sequence: $Cl_2/NaOH/Cl_2+ClO_2/NaOH/ClO_2/NaOH/ClO_2$

	Bleaching stage			Finally bleached pulp		
Test No.	Pulp conc., percent	Time, min.	Rest-chlorine, g./kilo pulp	Brightness, percent SCAN	Viscosity, cp. Tappi	Speck area, mm.²
3,835	3.5	60	6.20	90.1	50.8	10.3
3,836	3.5	180	4.69	90.9	48.7	3.9
3,837	10	60	2.27	90.6	50.2	2.4
3,838	10	180	1.59	91.6	47.3	1.9

The results in Tables 2 and 3 show how a significant reduction in the speck area and increased brightness of the pulp are obtained by treating the pulp with excess chlorine at elevated mass concentration in the third bleaching stage, without extra costs for heat or chemicals. Further, it can be seen from Table 2 how the addition of a small amount of ClO_2 to the chlorination process in the third bleaching stage improves the viscosity of the finally bleached pulp.

When treating the pulp according to the invention it should be seen that an amount of chlorine well sufficient for the excess chlorinating treatment is added to the prebleached pulp, preferably so that the amount of residual chlorine reaches at least 2 grams per kilogram pulp, e.g. 2–10 grams per kilogram pulp.

The results in Examples 2 and 3 also show that whilst retaining the size of the bleaching equipment and maintaining the pulp production by raising the pulp concentration and extending the bleaching time when bleaching prebleached pulp with Cl_2+ClO_2 it is possible to reduce the speck area of the finally bleached pulp to a mere tenth of that which is obtained in the case of lower pulp concentration and correspondingly shorter bleaching times.

What is claimed is:

1. A process for bleaching cellulose pulp in a sequence of bleaching stages with intermediate alkali treatment stages, comprising treating the pulp with chlorine in a first chlorine bleaching stage at low pulp concentration whereby during said chlorine bleaching stage and the subsequent alkali treatment stage, the major portion of the lignin content of said pulp is removed, then treating the pulp in a second chlorine bleaching stage at a pulp concentation of not less than 5% and a temperature of below 35° C. with an excess of chlorine, and thereafter treating the pulp with chlorine dioxide in at least one further bleaching stage.

2. The process according to claim 1 in which the pulp concentration in said second chlorine bleaching stage is between 5 to 13%.

3. The process according to claim 2 in which the temperature in the second chlorine bleaching stage is 20–30° C.

4. The process according to claim 1 in which a small quantity of chlorine dioxide is mixed with the excess chlorine in the second chlorine bleaching stage.

5. The process according to claim 4 in which the quantity of chlorine dioxide, estimated as active chlorine, comprises 0.5–2 grams per kilo of pulp in said second chlorine bleaching stage.

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