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HYPOCHLORITE SULFAMIC ACID PROCESS OF BLEACHING CELLULOSIC MATERIALS

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This invention relates to a process of bleaching cellulosic materials, particularly wood pulps, with an agent containing an inorganic hypochlorite and sulfamic acid.

In the papermaking art it is usual practice to bleach the pulp stepwise. First, the pulp is treated with chlorine. Next it is neutralized with sodium hydroxide. It then is bleached with hypochlorite. In particular instances this may be followed by further alkaline extraction and hypochlorite treatments or any other of a number of bleaching agents which include chlorine dioxide and hydrogen peroxide.

The present invention is based upon the discovery that in the foregoing sequence the hypochlorite bleaching step advantageously may be applied using as the bleaching agent a mixture of inorganic hypochlorite and sulfamic acid. It is believed that these two materials combine with each other, forming N-chlorosulfamic acid and N,N-dichlorosulfamic acid. In the presence of water and bleachable materials the latter two compounds decompose, forming hypochlorous acid and regenerating the sulfamic acid. The hypochlorous acid then is the source of nascent oxygen, which is the active bleaching agent, released in a relatively slow and controlled manner.

The net result is that there is more efficient utilization of the chlorine than otherwise would be the case. In fact, the amount of hypochlorite required to attain a predetermined level of bleaching is but 40–80% of that required in the absence of sulfamic acid.

In addition, the bleaching operation is carried out at a pH substantially lower than normal and yields a pulp of materially higher viscosity and strength. These important advantages are achieved, moreover, without the material degradation of the cellulose usually found at a lower pH, and while obtaining even better process control than usually is possible.

Considering the foregoing in greater detail:

The process of the invention is applicable to the bleaching of all cellulosic materials which are bleachable by treatment in an aqueous medium with inorganic hypochlorite. It is particularly applicable to the bleaching of papermaking and other cellulosic pulps such as coniferous and deciduous sulfite and kraft pulps, and high alpha specialty pulps.

A variety of inorganic hypochlorite bleaching agents may be used for bleaching the cellulosic material. Illustrative are sodium hypochlorite, potassium hypochlorite, calcium hypochlorite, calcium chloride hypochlorite (bleaching powder), and magnesium hypochlorite, sodium hypochlorite and calcium chloride hypochlorite being preferred members of the group.

As indicated above, the amount of hypochlorite bleaching agent which need be employed to accomplish a given degree of bleaching is substantially less than the amount normally required. Thus a hypochlorite use which is sufficient to supply but from 5–20 pounds of chlorine per ton of pulp (air dry basis) is sufficient when bleaching ordinary commercial sulfite and kraft pulps. The chemical saving achieved thus is quite impressive, being of the order of from 40–80%. This obviously reduces quite materially the cost of the chemicals required for the bleaching operation.

The amount of sulfamic acid required for use together with the hypochlorite is somewhat variable, depending upon the particular application. In general, from 1–50%, preferably 3–25% by weight of sulfamic acid is employed, based on the weight of available chlorine in the hypochlorite bleaching agent. At least 1% should be used in order to derive an advantageous effect from its use. However, if too much sulfamic acid is employed, it tends to tie up the chlorine, making it unavailable for the bleaching reaction.

It is a particular advantage of the presently described process that it may be carried out without significant modification of the equipment and procedure conventionally used for hypochlorite bleaching. Thus the preliminary stages of the bleaching reaction, i.e., the chlorine bleach and neutralization stages may be carried out in the usual manner. The hypochlorite bleaching stage then is carried out in a conventional batch or continuous reactor, adding the sulfamic acid in the desired quantity to the hypochlorite feed line, in order to insure good mixing and stabilization of the chlorine before the bleaching chemical contacts the pulp. If desired, however, particularly for sustained runs, the sulfamic acid may be added directly to the bleach liquor in the storage tank.

The reaction conditions prevailing in the reactor are approximately those conventionally prevailing, with the exception that the pH of the reaction mixture is maintained at a substantially lower level. Contrary to conventional bleaching, minimum degradation of the pulp occurs and maximum strength is retained at this pH level.

Thus the pulp present in the bleaching cell may have a consistency of from 3 to 16%. Conventional operating temperatures may be employed, e.g., temperatures of from the freezing point of the aqueous pulp to 70° C. The applicability of this process is not restricted by consistency or temperature. Any level of these conditions which could be used in conventional hypochlorite bleaching would be compatible with the sulfamic acid process. The duration of bleaching is that which is sufficient to obtain the predetermined brightness level of the pulp and may be, for example, in the case of a typical sulfite pulp, from ¼ to 4 hours.

Initial pH of the pulp in the reactor may be 8 to 10, while the final or dump pH may be as low as 6 to 9. In spite of the lower final pH, final pulp viscosities (1% CED, TAPPI Method 230) on the other hand are relatively high, being from 150–400 for typical sulfite pulps and from 150–250 for typical kraft pulps. This in turn indicates a Burst Factor which is 4–6 points higher on TAPPI handsheets than in the case of runs identical in all respects except for using the conventional amount of caustic buffered hypochlorite and omitting the sulfamic acid.

The progress of the invention is illustrated in the following examples, wherein physical test values of Burst Factor, Tear Factor, and Fold represent handsheets formed at 550 cc. Schopper-Reigler freeness and tested according to TAPPI methods T200ts–61, T220m–60, and T423m–50. Beating time is that required to reach the 550 cc. freeness level.

Example 1

This example illustrates the application of the process of the invention to the bleaching of coniferous sulfite wood pulp.

Two batches of commercial papermaking sulfite hemlock pulp were bleached in the conventional manner with chlorine, followed by neutralization with caustic soda. One of the batches then was subjected to the conventional calcium hypochlorite bleaching treatment; the other to the herein described calcium hypochlorite-sulfamic acid bleaching treatment.

In both instances the material was introduced into a conventional commercial bleaching reactor and the bleaching treatment carried out at a temperature of 36° C. over a time period of 2¾ hours. At the conclusion of the treatment both samples, undried, were subjected to the standard physical tests with results as follows:

	Control	Sulfamic Acid
Calcium Hypochlorite (as Cl_2, lbs./ton)	20.0	8.0
Sulfamic Acid (lbs./ton)	0.0	0.56
Final pH	8.60	7.45
Final Brightness	90.5	89.8
Final Viscosity (cps.)	125	356
Burst Factor	64.2	70.4
Beating Time	51	61
Tear Factor	82.5	89.0
Fold (M.I.T.)	920	1,360

Example 2

This example illustrates the application of the process of the invention to the bleaching of hardwood sulfite pulp.

The procedure of Example 1 was repeated, but using a papermaking western red alder sulfite pulp. The bleaching agent was calcium hypochlorite used at 34° C. over a bleaching period of about one hour and 15 minutes. The results of tests run on undried pulp were as follows:

	Control	Sulfamic Acid
Calcium Hypochlorite (As Cl_2, lbs./ton)	15.0	8.0
Sulfamic Acid (lbs./ton)		0.6
Final pH	9.5	8.40
Final Brightness	93	92.6
Final Viscosity (cps.)	150	374
Burst Factor	42.6	47.2
Beating Time	95	110
Tear Factor	69.5	73.7
Fold (M.I.T.)	60	110

Example 3

This example illustrates the application of the process of the invention to the bleaching of a commercial kraft pulp.

The procedure of Example 1 was repeated with the exception that a commercial kraft pulp was employed which was a mixture of hemlock, Douglas fir and cedar. The bleaching temperature was 32° C. and the time was one hour. The results of tests run on finished dried pulp are shown below:

	Control	Sulfamic Acid
Sodium Hypochlorite (As Cl_2, lbs./ton)	32.0	16–18
Sulfamic Acid (lbs./ton)		1.6
Final pH	9.5	6.9
Final Brightness	89.3	89.7
Final Viscosity (cps.)	154	171–197
Burst Factor	89.4	88.6
Beating Time	105	108
Tear Factor	117.9	116.7
Fold (M.I.T.)	2,220	1,610

It is apparent from an analysis of the data of the foregoing examples that the use of sulfamic acid in conjunction with the hypochlorite bleaching agent very materially reduces the amount of bleaching agent required to bleach the pulp to a predetermined brightness level. At the same time the strength of the pulp is actually increased, without adversely affecting its other properties.

Having thus described the invention in preferred embodiments, what is claimed as new and described to protect by Letters Patent is:

1. The process of bleaching cellulosic materials which comprises reacting the cellulosic material in finely divided form and in an aqueous medium with a bleaching quantity of an inorganic hypochlorite bleaching agent and from 1–50% by weight, based on the weight of available chlorine in said bleaching agent, of sulfamic acid, the reaction being carried out until the predetermined degree of bleaching of the cellulosic material has been obtained.

2. The process of bleaching cellulosic papermaking pulps which comprises treating an aqueous pulp slurry with a bleaching quantity of an inorganic hypochlorite bleaching agent and from 3–25% by weight, based on the weight of the available chlorine in said bleaching agent employed, of sulfamic acid, the bleaching treatment being carried out at a temperature of from the freezing point of the aqueous pulp to 70° C., for a time adequate to bleach the pulp to the predetermined brightness level.

3. The process of claim 2 wherein the inorganic hypochlorite comprises sodium hypochlorite.

4. The process of claim 2 wherein the inorganic hypochlorite comprises a calcium hypochlorite.

5. The process of claim 2 wherein the hypochlorite bleaching agent is used in amount sufficient to supply from 5–20 pounds of chlorine per ton of air dry cellulosic pulp.

6. The process of claim 2 wherein the aqueous pulp slurry has a pH of from 8–10 at the beginning of the bleaching reaction and a pH of from 6–9 at the completion of the bleaching reaction.

7. The process of claim 2 wherein the aqueous pulp slurry has a consistency of from 3 to 16%.

8. The process of bleaching sulfite papermaking pulps which comprises treating the aqueous pulp slurry at a consistency of from 3 to 16% with an amount of calcium hypochlorite sufficient to supply from 5–20 pounds of chlorine per ton of air dry pulp, and from 3–25% by weight, based on the weight of the available chlorine in the calcium hypochlorite, of sulfamic acid, the bleaching treatment being carried out at a temperature of from the freezing point of the aqueous pulp to 70° C. and at an initial pulp pH of from 8–10 for a time sufficient to bleach the pulp to the predetermined brightness level.

9. The process of bleaching kraft papermaking pulp which comprises treating the aqueous pulp slurry at a consistency of from 3 to 16% with an amount of sodium hyprochlorite sufficient to supply from 5–20 pounds of chlorine per ton of air dry pulp and from 3–25% by weight, based on the weight of the available chlorine in the sodium hypochlorite, of sulfamic acid, the bleaching treatment being carried out at a temperature of from the freezing point of the aqueous pulp to 70° C. and at an initial pulp pH of from 8–10 for a time sufficient to bleach the pulp to the predetermined brightness level.

10. The process of bleaching a high alpha specialty sulfite pulp which comprises treating the aqueous pulp slurry at a consistency of from 3 to 16% with an amount of calcium hypochlorite sufficient to supply from 5–20 pounds of chlorine per ton of pulp (air dry weight basis) and from 3–25% by weight, based on the weight of the available chlorine in the calcium hypochlorite, of sulfamic acid, the bleaching treatment being carried out at a temperature of from the freezing point of the aqueous pulp to 70° C. and at an initial pulp pH of from 8–10 for a time sufficient to bleach the pulp to the predetermined brightness level.

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