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## USE OF SULFAMIC ACID IN CHLORINATION STEP OF MULTISTAGE BLEACHING PROCESS

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This invention relates to the bleaching of paper pulp. More particularly, this invention refers to an improvement in the use of sulfamic acid in paper pulp bleaching operations carried out with chlorine, hypochlorite or hypochlorous acid.

The main objective in bleaching wood pulp is to obtain a white pulp with stable color and with a minimum deleterious effect on physical and chemical properties of the pulp.

Wood pulp such as kraft, sulfite, etc., for use in making paper is customarily bleached in a series of steps, generally referred to as the "Multistage Bleaching" process. This process involves pulp bleaching and purification wherein the various impurities in the fiber are removed in a gradual and orderly way in a series of stages without serious degradation of the fiber in any one stage.

The first stage is a chlorination of the pulp at very low pH, such as 1 to 2. In this first stage most of the residual lignins are chlorinated, ordinarily using from 5 to 7% chlorine concentration, expressed as available chlorine based on the weight of the pulp. The second stage involves a caustic extraction wherein the substitution products formed in the first stage are solubilized and washed out. The third stage or hypochlorite stage is a true bleaching stage wherein hypochlorite solutions at pH between 8 and 11 are employed. Ordinarily, hypochlorite concentration from 0.5 to 2%, expressed as available chlorine based on the weight of the pulp, and temperatures of 30° to 40° C. for a period of 1 to 5 hours will be used in the third stage.

According to the present invention, I have found an improvement in pulp bleaching operations whereby one can obtain outstanding pulp brightness with minimum degradation or loss of strength of the pulp.

In the present invention, a critical amount of sulfamic acid is admixed with the pulp being treated in the first stage of the pulp bleaching operation. The amount will be from 5 to 20% by weight, based on the weight of the available chlorine in the first stage operation.

For some reason, the use of this small but important amount of sulfamic acid in the first bleaching stage helps to produce pulp of excellent brightness and improved tear, bursting and tensile strength.

In a preferred aspect of the present invention, sulfamic acid in a critical amount is also used in the third stage of the pulp bleaching operation. The amount will be from 1 to 30% and preferably 5 to 20% by weight, based on the weight of the available chlorine in the third stage.

In this third stage, temperatures of 30° to 80° C. are satisfactory but I prefer a temperature in the range from 55° to 75° C. A pH of 6 to 11 can be used. Bleaching times of 1 to 3 hours will normally be employed.

Instead of sulfamic acid itself, an alkali or alkaline earth or ammonium salt can be used. Sodium, potassium, calcium, lithium and ammonium salts are particularly useful. Amounts should be calculated on an acid equivalent basis.

It is surprising that, using the small but critical amount of sulfamic according to this invention, one can obtain high brightness pulps having an improved viscosity of 200% or higher compared with pulp treated identically except without the use of the specified amount of sulfamic. It is generally recognized that there is a direct correla-

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tion between viscosity and tear, bursting and tensile strength. A standard strength test involves dissolving the pulp in cupriethylene diamine and measuring the viscosity of the resulting solution (TAPPI Standard T-230 Sm-50). Brightness can be measured according to standard tests (TAPPI Standard T-217 657 m-48).

If desired, the pulp can be additionally treated with a second hypochlorite stage and/or with other oxidizing agents such as hydrogen and/or sodium peroxide, chlorine dioxide, and the like, as will be readily understood.

This invention will be more fully understood by reference to the following illustrative examples:

### Example 1

Thirty grams of unbleached oven-dried paper pulp are mixed with 2,000 milliliters of water and disintegrated in a Herrmann disintegrator for 30 minutes. The pulp is then filtered through a Buchner funnel and placed into a polyethylene bag. Separately, 40 milliliters of aqueous chlorine solution (2 grams of available chlorine) are dissolved in 760 milliliters of water, mixed with 0.2 gram of sulfamic acid, and added to the pulp. The bag is closed with a rubber band and kneaded by hand for several minutes to insure uniform distribution of the contents. A consistency of about 4% and a pH of about 2 is obtained. The bag is kept in a constant temperature water bath at 22° C. for 60 minutes, repeating the kneading every 10 minutes.

The pulp is removed from the bag, filtered in a Buchner funnel, and placed in an empty polyethylene bag where it is mixed with a solution of 2 grams of sodium hydroxide dissolved in 250 milliliters of water (consistency of about 12%). The bag is then closed as before, kneaded for 2 minutes and placed in a water bath at 60°–80° C. for 1 hour, repeating the kneading every 10 minutes.

The pulp is removed from the bag, rinsed with distilled water, filtered in a Buchner filter and placed in an empty polyethylene bag. Separately, 15 milliliters of sodium hypochlorite solution (0.75 gram of available chlorine which is 2.5% of available chlorine based on the weight of the pulp) are dissolved in 200 milliliters of distilled water and added to the pulp. Drops of sodium hydroxide solution are added to obtain a pH between 10 and 11. The bag is closed with a rubber band, kneaded for 2 minutes and placed in a water bath at 60° C. for 90 minutes, repeating the kneading every 10 minutes.

The pulp is removed from the bag, filtered in a Buchner funnel, and washed with distilled water until a neutral pH is obtained in the filtrate. Pulp brightness and strength are excellent, as determined by standard tests.

### Example 2

The preceding example is repeated except that 0.15 gram of sulfamic acid is admixed with the hypochlorite solution in the third stage of the operation. By these procedures, a bleached paper pulp has been readily obtained having a viscosity of 18.9 centipoises (0.5% Cu Ed viscosity brightness of 77.86 GE (TAPPI Standard T-217 m-48)).

The invention claimed is:

1. In the multiple stage chlorination bleaching of wood pulp which involves a first stage chlorination bleach of the pulp at pH 1–2, a second stage extraction with caustic, and a third stage hypochlorite bleach at pH 6–11 and a temperature of 30° to 80° C. for 1 to 3 hours, the process improvement of admixing with the pulp in said first stage bleach from 5 to 20% by weight of a compound selected from the group consisting of sulfamic acid and its alkali, alkaline earth and ammonium salts calculated on an acid equivalent basis and based on the weight of the available chlorine in said first stage bleach.

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2. The process as set forth in claim 1 wherein there is admixed with the pulp in said third stage bleach from 1 to 30% by weight of a compound selected from the group consisting of sulfamic acid and its alkali, alkaline earth and ammonium salts, calculated on an acid equivalent basis and based on the weight of the available chlorine in said third stage bleach.

3. The process as set forth in claim 2 wherein said compound is sulfamic acid.

4. The process as set forth in claim 2 wherein said compound is sodium sulfamate.

5. The process as set forth in claim 2 wherein said compound is ammonium sulfamate.

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6. The process as set forth in claim 2 wherein said temperature is 55° to 75° C.

7. The process as set forth in claim 2 wherein the amount of said compound used in said third stage is from 5 to 20% by weight, calculated as specified.

#### References Cited by the Examiner

##### UNITED STATES PATENTS

3,177,111 4/1965 Larsen ----- 162—73

DONALL H. SYLVESTER, *Primary Examiner*.

HOWARD R. CAINE, *Examiner*.