United States Patent

25 et al.

[15] 3,653,804

[45] Apr. 4, 1972

[54] BLEACHING OF WOOD PULP WITH DITHIONITE SOLUTION STABILIZED BY ZINC COMPOUND

[72] Inventors: **Alfons Janson**, Ludwigshafen, Rhine, **Franz Poschmann**, Limburgerhof Pfalz; **Georg Wittmann**, Ludwigshafen, Rhine, all of Germany

[73] Assignee: **Badische Anilin- & Soda-Fabrik Aktiengesellschaft**, Ludwigshafen, Rhine, Germany

[22] Filed: **Dec. 26, 1967**

[21] Appl. No.: **693,280**

[30] **Foreign Application Priority Data**

Dec. 31, 1966 Germany ..... P 15 46 239.2

[52] **U.S. Cl.** **8/110**, 162/83, 252/105, 252/188

[51] **Int. Cl.** **D06l 3/10**, D21c 9/10, C11d 7/54

[58] **Field of Search** 8/110; 252/105, 188; 162/82, 162/83; 23/129

[56] **References Cited**

UNITED STATES PATENTS

2,071,307	2/1937	Hirschkind	162/83 X
2,707,144	4/1955	Sparrow et al.	162/83 X
3,207,694	9/1965	Gogek	252/105
3,287,276	11/1966	Poschmann et al.	252/105
1,710,310	4/1929	Helwig	252/188
1,810,665	6/1931	Kritchevsky et al.	252/188

FOREIGN PATENTS OR APPLICATIONS

492,589	9/1938	Great Britain	252/105

OTHER PUBLICATIONS

Ingruber and Kopanidis, " Hydrosulphite Bleaching Part 1," Pulp and Paper Magazine of Canada, 68(6), T258– T267 (1967)

Primary Examiner—Mayer Weinblatt
Assistant Examiner—D. Silverstein
Attorney—Marzall, Johnston, Cook & Root

[57] **ABSTRACT**

Use of sparingly soluble zinc compounds for prolonging the stability of wood pulp bleaching solutions containing dithionites.

2 Claims, 5 Drawing Figures

FIG. 1

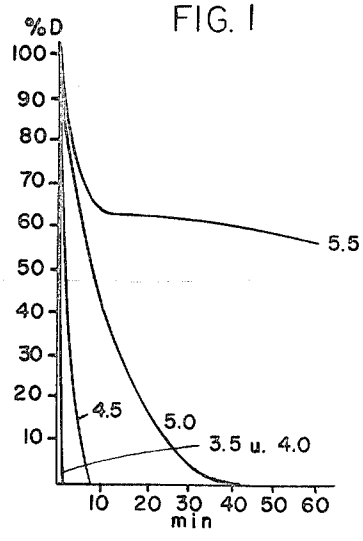


FIG. 2

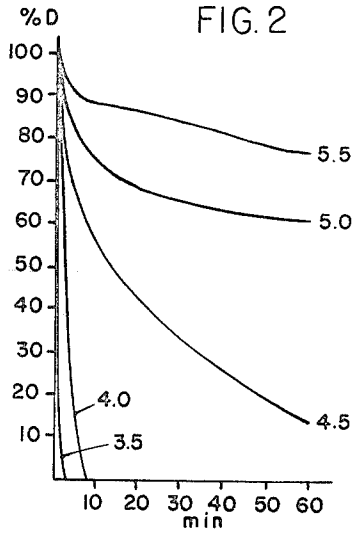


FIG. 3

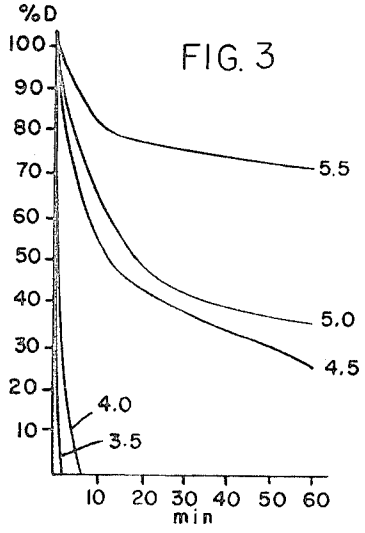


FIG. 4

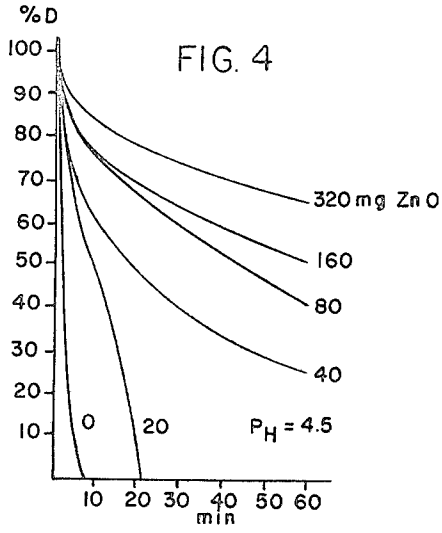
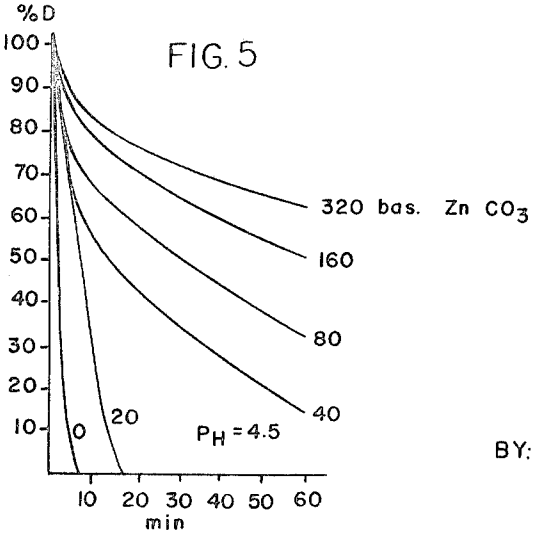


FIG. 5



INVENTORS:
ALFONS JANSON
FRANZ POSCHMANN
GEORG WITTMANN

BY: Marzall, Johnston, Cook & Root
ATT'YS

BLEACHING OF WOOD PULP WITH DITHIONITE SOLUTION STABILIZED BY ZINC COMPOUND

The invention relates to an improved method of bleaching with dithionites in a weakly acid range. More particularly, it relates to a method of bleaching in the presence of substances by which the stability of the dithionites in the bleaching solution is prolonged.

For many years dithionites, particularly sodium dithionite and zinc dithionite, have been used for reducing bleaching. These two dithionites have been used on a large scale in the pH range of from 4 to 7 for bleaching wood pulp and cellulose.

Dithionites are substances which have high reducing power and are therefore easily oxidized. Moreover they have high sensitivity to acids so that when they are used in the aqueous phase at a pH value of 6 attack caused by hydrogen ions is distinct and at a pH value of 4 the dithionites are completely destroyed by hydrogen ions in only a few minutes. Destruction of the dithionite by hydrogen ions results in the development of hydrogen sulfide, if only in traces, and this increases as the pH value falls. Traces of heavy metals promote the destruction of dithionites. Solid dithionites have high sensitivity to traces of water and also tend to undergo internal decomposition when stored in closed vessels.

For these reasons, substances which will protect dithionites against destruction have been sought for a long time. It is known that solid dithionite which undergoes only slight internal decomposition in closed vessels can be obtained by mixing 1 to 2 percent of zinc dust with the dithionite solution prior to separation of the dithionite or with the already separated dithionite. It is also known that anhydrous sodium dithionite obtainable by drying can be brought into a form having much improved stability in the air by adding 5 to 10 parts of calcined sodium carbonate or powdered sodium hydroxide or powdered calcium oxide to dithionite containing water of crystallization prior to its being dried, or during the drying or to the dried sodium dithionite.

Zinc dithionite is usually obtained in very finely divided form so that the product causes dust nuisance and leads to bridge formation. If zinc chloride is used for salting out in the production of fine crystallized zinc dithionite, there is a tendency for the zinc dithionite to decompose because zinc chloride is fairly acid in aqueous solution. It has therefore been proposed in the production of non-dusting crystalline zinc dithionite which does not tend to form bridges to add, during evaporation of zinc dithionite solutions, 2 to 10 percent by weight (with reference to the zinc dithionite contained in solution) of glycerine and about 0.2 to 0.8 percent by weight of a stabilizing agent containing zinc, such as zinc dust, zinc oxide, zinc carbonate or another basic compound containing zinc, prior to commencement of the evaporation process, the solutions being evaporated having a pH value of 3.6 to 4.4.

Furthermore it is known that weak alkali and sodium sulfite are effective stabilizers for dithionites. Alkali metal phosphates and alkali metal polyphosphates, the alkali metal salts, alkaline earth metal salts and ammonium salt of ethylenediaminetetracetic acid and free ethylenediaminetetracetic acid, and also alkali metal citrates and alkali metal tetraborates have also been proposed as additives to dithionites in order particularly to bind heavy metal ions in the bleaching of wood pulp in the weakly acid range, because better bleaching effects are then obtained.

We have now found that in bleaching in a weakly acid pH range, preferably at a pH value of from 4 to 6, with water-soluble dithionites, the solutions have considerably prolonged stability when the operation is carried out in the presence of sparingly soluble zinc compounds. Examples of suitable compounds are zinc oxide, zinc hydroxide, zinc carbonate, basic zinc carbonate, basic zinc silicate and basic zinc phosphate. Mixtures of these compounds are similarly effective.

It is advantageous to add the zinc compounds to the bleaching liquor in an amount of at least 5 percent by weight with reference to the dithionite added.

The zinc compound may be added to the dithionite prior to addition of the latter to the bleaching mixture. Addition of the sparingly soluble zinc compounds (which are capable of adsorbing hydrogen sulfide and sulfur dioxide) to the solid dithionite improves the odor when the solid dithionites are stored.

For the two known types of pulp (namely groundwood pulp which is formed by simple grinding of wood, and chemical pulp which is made by first clipping the wood and then softening the chips with chemical reagents, as for example sodium sulfite, at elevated temperature and pressure) the best bleaching effect is achieved in the pH range of from about 4.0 to 6.0, because bleaching at pH values of 7or more results in yellowing of the pulp.

Bleaching of both types of pulp is carried out at about 60° C. with addition of dithionites. On a commercial scale it lasts about 15 minutes. The most favorable results are obtained by carrying out bleaching for about 1 hour provided the reducing agent remains active during the whole period.

A consistency (i.e., content of dry fiber) of 0.5 to about 12 percent by weight, preferably from 2 to 4 percent by weight, is used in the bleaching of groundwood pulp and usually about 0.5 to 1.0 percent by weight (with reference to the amount of dry fiber) of dithionite is added as bleaching agent. This means that in 1 liter 20 to 40 g. of wood fiber is suspended and that at the beginning of the bleaching the amount of dithionite added, either as solid or as solution, is such that 200 to 400 mg. of dithionite is present per liter at the commencement of bleaching.

The durability of sodium dithionite for this concentration of bleaching agent is indicated below without additions and with additions of sparingly water-soluble zinc compounds in buffer solutions of the Michaelis buffer acetic acid, sodium acetate. The pH value of 3.5 to 5.6 can be kept constant, depending on the mixing ratio, by mixtures of 0.2N acetic acid solution and 0.2N sodium acetate solution (G.S. Walpole, Biochem. J. 105, 2501 and 2521 (1914); G. Gottschalk, Z. analyt. Chem., 167, 342 (1959). The buffer is not attacked by dithionites. Durability is investigated under nitrogen at 60.0 ±0.5° C. and the content of sodium dithionite is determined in dependence on pH value and on time by titration according to the indigo carmine method (A. Binz, H. Bertram, Angew. Chem., 18, 168 to 170 (1905).

In FIGS. 1 to 4 of the drawings D means "dithionite."

FIG. 1 of the drawings shows the durability of a solution of 400 mg. of sodium dithionite per liter in dependence on the pH value of the buffer solution and on time. Four hundred milligrams of sodium dithionite is made equal to 100 percent. The curve for pH 4.5 shows for example that the 400 mg. of sodium dithionite was destroyed in only 6 minutes.

FIG. 2 shows the durability of a solution of 400 mg. of sodium dithionite in the presence of 40 mg. of basic zinc carbonate. It is seen that at pH 4.5 14 percent of the sodium dithionite used is still present after 1 hour.

FIG. 3 shows the durability of a solution of 400 mg. of sodium dithionite in the presence of 40 mg. of zinc oxide. Twenty four percent of the dithionite added is still present after 1 hour at pH 4.5.

FIGS. 4 and 5 show the effect of increasing amounts of zinc oxide and basic zinc carbonate on 400 mg. of sodium dithionite per liter at a pH value of 4.5. The amounts of zinc oxide or basic zinc carbonate used per liter are 20, 40, 80, 160 and 320 mg. The curve 0 illustrates the conditions without any additive.

The Figures show that increasing amounts of zinc oxide or basic zinc carbonate have a progressively increasing effect on the durability of sodium dithionite.

Degradation of sodium dithionite with an addition of 20 mg. of zinc oxide (equal to 5 percent with reference to 400 mg. of sodium dithionite) requires 21 minutes and with an equivalent addition of basic zinc carbonate 16 minutes, whereas sodium dithionite without additive is destroyed after only 6 minutes. Surprisingly this effect is not observed in the case of zinc acetate or other water-soluble zinc salts. It evidently requires the solid phase of a sparingly soluble zinc compound to bind

traces of hydrogen sulfide formed, whereas in the case of zinc acetate the solubility product first has to be exceeded before sulfide ions can be bound from the solution. Sulfide ions have a strongly destructive effect on dithionites in the weakly acid pH range.

The favorable effect of the additives on the result of the bleaching is clear from a comparison of bleachings of wood pulp with sodium dithionite which have been carried out with an addition of a sparingly soluble zinc compound and without such an addition. The series of experiments given in Table 1 apply to the bleaching of wood pulp having a consistency of 2 percent at 60° C., a pH value of 4.5 and a period of 1 hour with a concentration of bleaching agent of 0.5 to 1.0 percent with reference to the dry solids. The whiteness of the sheets obtained is determined with an Elrepho spectrophotometer, filter R 46T (Zeiss, Oberkochen). The unbleached pulp has a whiteness of 59.4.

TABLE 1

% with reference to bleaching agent of	whiteness achieved with % bleaching agent 0.5%	1.0%
zinc oxide		
0	64.0	66.4
5	64.8	68.6
10	65.2	69.4
basic zinc carbonate		
0	64.0	66.4
5	64.6	68.4
10	65.4	69.2

The favorable effect of additions of sparingly soluble zinc compounds on the bleaching process in the weakly acid range is maintained even in the case of sodium dithionite which has been stabilized by small additions of urea against spontaneous thermal decomposition upon the action of water or by small additions of macromolecular substances, such as polyacrylamide or sodium polyacrylate, against thermal decomposition.

The use of additions of sparingly soluble zinc compounds also has the advantage that discoloration and corrosion by hydrogen sulfide are avoided and for example in the bleaching of wood pulp, action of hydrogen sulfide on the bronze screen used after bleaching in the separation of the pulp.

We claim:

1. In a process for bleaching wood pulp in aqueous suspension with sodium dithionite in the weakly acid range the improvement which comprises the carrying out bleaching at a pH value of 4 to 6 in the presence of a sparingly soluble substance in solid phase selected from the group consisting of zinc oxide, zinc hydroxide, zinc carbonate, basic zinc carbonate, basic zinc silicate and basic zinc phosphate, in an amount of at least 5 percent by weight with reference to the sodium dithionite added.

2. In a process as claimed in claim 1, the step of adding the zinc compound to the sodium dithionite prior to addition to the bleaching mixture.

* * * * *