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3,462,344

## SUPERBLEACHING OF WOOD PULPS

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No Drawing. Filed May 31, 1966, Ser. No. 553,667

Int. Cl. D21c 9/16, 9/10

U.S. Cl. 162—72

12 Claims

### ABSTRACT OF THE DISCLOSURE

An improved hydrogen peroxide superbleach process for primary-bleached chemical or semichemical wood pulp is provided by adding N-benzoyl succinimide to the aqueous bleaching system. This allows operation at a much lower pH than is normally necessary and reduces the amount of hydrogen peroxide necessary to achieve the desired final brightness.

This invention relates to the superbleaching of wood pulps, and particularly to the superbleaching of chemical and semichemical wood pulps.

The demand for pure and bright wood pulps has resulted in the development of very effective chemical and semichemical pulping processes. Typical processes are the kraft process, the sulfite process, the soda process and the neutral sulfite semichemical process, each of which is designated for a particular kind of pulp and to provide particular properties.

The purified pulps provided by these pulping methods generally are bleached to a high reflectance, or brightness, and various so-called primary-bleaching processes employing chlorine-containing chemicals have been devised which bleach the pulp to brightnesses of on the order of 75 to 90% on the well-known GE brightness scale. In order to provide even higher brightnesses, generally 1 to 5 percentage points higher than the primary-bleached brightness levels, it has become common practice to treat the primary-bleached pulp with a hydrogen peroxide solution. This additional bleaching operation is known in the trade as superbleaching.

While the hydrogen peroxide superbleaching process is highly effective, it has been desired to achieve an effective superbleach with less active oxygen than is required in the processes used heretofore. Furthermore, many typical superbleaching operations, for example the tower superbleach process which is operated with an aqueous slurry of pulp and hydrogen peroxide, are carried out at a pH of 10.5 or even higher in order to assure effective bleaching. Since subsequent use of the pulp generally requires that it be at a neutral to acid pH, it is necessary to employ a neutralization step to bring pulps bleached at such elevated pH's to a satisfactory use condition.

It therefore has been desired, and it is an object of our invention, to improve the effectiveness of hydrogen peroxide in superbleaching primary-bleached pulps thereby permitting use of less of this active oxygen chemical, and also to modify the hydrogen peroxide superbleach in a fashion which makes it possible to carry it out at essentially neutral pH where desired.

We have now found that we are able to achieve these desirable objectives by superbleaching a pulp which has been primary-bleached with typical chlorine-containing

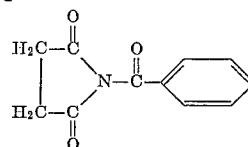
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bleaching chemicals, with as little as 0.01 to 0.5%, and preferably 0.03 to 0.25%, by weight of hydrogen peroxide based on the weight of the dry pulp, provided there is present in the superbleaching system 0.01 to 3%, and preferably 0.1 to 1%, by weight of N-benzoyl succinimide based on the dry weight of the pulp. Our improved superbleaching operation is carried out at a temperature of 75° to 212° F., and preferably 120° to 160° F., over a period of 15 minutes to 16 hours, and preferably 2 to 4 hours, with the pulp being at a consistency of 2 to 85%, and preferably 6 to 25%, and the pH of the pulp being 2.5 to 9.5, and preferably 6 to 8.

Desirably a molecularly dehydrated phosphate, for example sodium tripolyphosphate, tetrasodium pyrophosphate, tetrapotassium pyrophosphate or sodium hexametaphosphate is present in the superbleaching system in an amount up to 1% by weight, and preferably 0.25 to 0.5% by weight. It is often useful also to have present in the system an alkali such as sodium carbonate or sodium hydroxide in an amount up to 0.5% by weight, and preferably 0.05 to 0.25% by weight, and magnesium sulfate in an amount up to 0.1% by weight. All of the weights given herein are based on the dry weight of the pulp.

Use of our N-benzoyl succinimide additive in the hydrogen peroxide superbleaching operation results in a synergistic reduction in the amount of hydrogen peroxide required for adequate superbleaching and furthermore makes it possible to bleach at a much lower pH than is normally necessary in the absence of our additive. For example, brightnesses fully as high as those obtained with 0.25% to 0.5% of hydrogen peroxide in the absence of our N-benzoyl succinimide have been achieved with amounts of hydrogen peroxide as low as 0.03% in the presence of our N-benzoyl succinimide additive. Furthermore, the pH required for bleaching with our additive present in the system can be as low as neutral or even lower, whereas with hydrogen peroxide in the absence of our N-benzoyl succinimide additive, the pH for optimum bleaching often is on the order of 10.5 or even higher.

Our superbleaching additive, N-benzoyl succinimide, has the following formula:



This additive is effective in promoting the superbleaching effect of hydrogen peroxide as it is applied to primary-bleached wood pulps, and is particularly useful in that it has no harmful effects on the pulps or products made from them. It is employed in our process in the amount of about 0.01 to 3% by weight based on the dry weight of the pulp, and preferably in the amount of 0.1 to 1% on that basis. Use of more than the upper amount of about 3% by weight is unnecessary since it does not add particularly to the effectiveness of hydrogen peroxide in superbleaching, whereas use of less than 0.01% does not result in a satisfactory improvement of the hydrogen peroxide superbleach.

The pulps superbleached in accordance with our process are the chemical and semichemical pulps, for example the kraft pulps, the sulfite pulps, the soda pulps and

the neutral sulfite semichemical pulps, prepared from typical hardwoods and softwoods, for example poplar, beech, spruce, pine, fir, birch, cherry and other woods commonly used in producing pulps. These pulps are prepared typically by reducing the wood to wood chips and treating the chips in the pulping process for a sufficient time, and at a temperature, which removes much of the non-cellulosic, generally ligneous, substances present in the wood. Removal of these non-cellulosic materials purifies the pulp considerably.

However, the pulps resulting from these treatments are not bright enough for many uses, and following their preparation they are bleached in typical primary-bleaching processes employing chlorine chemicals. Such primary-bleaching processes often involve several steps. Typical sequences are: a chlorine treatment, a caustic extraction and a hypochlorite bleach; a sequence embodying a chlorine treatment, a caustic extraction, a chlorine dioxide bleach, a caustic extraction and a chlorine dioxide bleach; a sequence embodying a chlorine treatment, a caustic extraction, a hypochlorite bleach and a chlorine dioxide bleach; a sequence embodying a chlorine treatment, a caustic extraction, a hypochlorite bleach, a chlorine dioxide bleach, a caustic extraction and a chlorine dioxide bleach; or a sequence of a chlorine treatment, a caustic extraction, a hypochlorite bleach, a chlorine dioxide bleach and a hypochlorite bleach. Alternatively, the primary-bleach may be carried out with any of the chlorine-containing chemicals alone if desired, or by other combinations of these chemicals than suggested above.

Our activated hydrogen peroxide superbleach is applied to pulps and papers at essentially any stage of production following the primary chlorine-chemical bleach. One useful technique involves treating the pulp in an aqueous slurry at a pulp consistency of on the order of 2 to 25 weight percent. Pulp consistency is calculated by the following formula:

$$\frac{\text{Dry pulp weight}}{\text{Wet pulp weight}} \times 100 = \text{Percent consistency}$$

Our activated hydrogen peroxide superbleach is likewise effective when carried out on a pulp web or paper sheet or on pulp crumbs, at any stage during drying, for example when the pulp consistency is about 25% to 85% by weight. In this manner of operation activated hydrogen peroxide solution preferably is applied in aqueous solution during drying of the pulp or paper.

It is desirable to employ a condensed phosphate, for example sodium tripolyphosphate, tetrasodium pyrophosphate, tetrapotassium pyrophosphate or sodium hexametaphosphate in our superbleach system since this additive improves its effectiveness. When employed, the phosphate is used in an amount of up to about 1%, and preferably of about 0.25 to 0.5%, based on the dry weight of pulp.

It is also useful in many cases to employ an alkali such as sodium carbonate or sodium hydroxide, in an amount up to about 0.5%, and preferably of about 0.05 to 0.25%, by weight based on the dry weight of the pulp. This additive is employed in order to adjust pH.

Another useful additive is magnesium sulfate, which may be employed in an amount up to about 0.1% by weight. This additive is useful for improving stability of the hydrogen peroxide against loss of active oxygen.

Other additives commonly employed in the bleaching of pulps and papers may be used in our process, for example sulfuric acid, sodium silicate and chelating agents such as the penta-sodium salt of diethylenetriamine pentaacetic acid or the like, where the useful properties of such additives are sought.

The hydrogen peroxide and N-benzoyl succinimide, together with other additives as desired, are contacted with the pulp or paper in the form of an aqueous solution, preferably premixed for ease of handling, at any concentration which provides the desired amount of the additives and the desired solids concentration of the pulp being treated.

Our superbleach is carried out at a temperature of about 75° to 212° F., and preferably of 120° to 160° F., for about 15 minutes to 16 hours, and preferably for 2 to 4 hours. The time is dependent upon temperature, with the elevated temperatures within the above range reducing the time required. Operation at higher temperatures than 212° F. is not recommended since such operation raises costs, whereas operation at temperatures below about 75° F. extends the time required for effective superbleaching. Operation for longer times than about 16 hours is not necessary, although it does not harm the pulp or paper while operation for less than about 15 minutes does not result in complete utilization of the hydrogen peroxide. Any residual hydrogen peroxide and N-benzoyl succinimide and the reaction products of the superbleach, may be left in the pulp or paper following the superbleach as they are not harmful to the pulp.

Our superbleaching operation is carried out in an aqueous system having an initial pH of 2.5 to 9.5, and preferably of 6 to 8. By this it is meant that the pulp or paper and the superbleach solution are at pH's within these ranges when the superbleach is commenced. The pH following bleaching, the final pH, is within the same overall range although it may vary slightly from the initial pH. pH's as low as 2.5 are effective with hydrogen peroxide activated with our N-benzoyl succinimide, whereas when pulp is superbleached with hydrogen peroxide alone, neutral to acid, or even slightly alkaline, pH's are not generally as effective as highly elevated pH's of on the order of 10.5 or higher.

The following examples are presented by way of illustration of our invention only, and are not to be considered as limiting the scope thereof in any way.

Percentages of ingredients given in the examples are weight percentages based on dry pulp weight. The GE brightness percentage figures given in these examples were determined employing a Gardner reflectometer with the brightness values being corrected to GE standards.

The wood pulps used in the examples were bleached by typical chlorine-chemical primary-bleaching processes identified in the examples. These processes employ well-known primary-bleaching steps which are defined fully in Pulp and Paper, Casey (vol. 1), Interscience Publishers, Inc., New York, 2nd ed., pp. 508-533. The sequences of steps are identified in the examples by code letters, C meaning a chlorine treatment, D a chlorine dioxide bleach, E a caustic extraction, and H a sodium hypochlorite bleach.

#### Example 1

Samples of a hardwood kraft pulp primary-bleached by a CEHDD bleaching sequence to a brightness of 89.9 were mixed with hydrogen peroxide solutions providing the amounts of hydrogen peroxide and N-benzoyl succinimide and the pH's shown in Table 1 which follows, at a pulp consistency of 12%, and permitted to stand for 4 hours at 140° F.

TABLE 1

Hydrogen peroxide, wt. percent	N-benzoyl succinimide, wt. percent	Initial pH	Final pH	Super bleached GE brightness, percent
Primary-bleached brightness.....				(89.9)
0.031.....	0.18	4.4	4.5	91.4
0.031.....	0.18	6.2	5.6	91.8
0.031.....	0.18	7.2	6.7	92.2
0.031.....	0.18	8.3	7.1	92.1
0.031.....	0.18	9.7	7.6	91.5

#### Example 2

This example compares the superbleaching effectiveness of our N-benzoyl succinimide activated hydrogen peroxide system with a hydrogen peroxide system containing much more hydrogen peroxide but not activated with N-benzoyl succinimide. Samples of the hardwood kraft pulp defined in Example 1 above and having a

primary-bleached brightness of 89.9% were treated as 12% consistency slurries at 140° F. for 4 hours. The additives employed in addition to the N-benzoyl succinimide are typical auxiliary ingredients and were used to provide the proper pH conditions for effective bleaching.

TABLE 2

Hydrogen peroxide, wt. percent	N-benzoyl succinimide, wt. percent	Other additives, wt. percent	Initial pH	Final pH	Super-bleached GE brightness, percent
Primary-bleached brightness.					(89.9)
0.031		0.5 sodium tripolyphosphate.	7.5	7.1	90.2
0.25		0.3 sodium hydroxide, 3.0 sodium silicate.	9.8	9.0	91.6
0.5		0.6 sodium hydroxide, 0.3 sodium silicate.	11.1	10.3	92.2
0.03	0.18	0.5 tetrasodium pyrophosphate.	7.2	6.7	92.2
0.03	0.18	0.1 sulfuric acid, 0.5 tetrasodium pyrophosphate.	6.2	5.6	91.8

## Example 3

This example demonstrates the effectiveness of our process on a softwood kraft pulp primary-bleached to a brightness of 86.6% in a CEHDED sequence. The superbleach was carried out at 12% pulp consistency, for 4 hours, at 140° F. The effectiveness of our N-benzoyl succinimide activated hydrogen peroxide is compared with the effectiveness of hydrogen peroxide not activated with our N-benzoyl succinimide additive, it being shown that much more hydrogen peroxide is required for superbleaching in the absence of N-benzoyl succinimide.

TABLE 3

Hydrogen peroxide, wt. percent	N-benzoyl succinimide, wt. percent	Other additives, wt. percent	Initial pH	Final pH	Super-bleached GE brightness, percent
Primary-bleached brightness.					(86.6)
0.06		0.1 sodium hydroxide, 2.0 sodium silicate.	10.3	9.4	88.5
0.75		0.5 sodium hydroxide, 2.0 sodium silicate.	10.8	9.9	91.0
1.0		0.8 sodium hydroxide, 2.0 sodium silicate.	10.9	10.1	91.7
0.025	0.15	0.1 sodium carbonate, 0.5 tetrasodium pyrophosphate.	9.0	7.6	91.4
0.06	0.37	0.25 sodium carbonate, 0.5 tetrasodium pyrophosphate.	9.5	8.1	91.9

The above examples demonstrate the effectiveness of a very small amount of hydrogen peroxide as a superbleach when it is activated with N-benzoyl succinimide in accordance with our invention. The examples also demonstrate that effective superbleaching with hydrogen peroxide can be carried out at quite low pH when N-benzoyl succinimide is employed in the superbleaching system, although it does not interfere with superbleaching at pH's as high as on the order of 9.5.

Pursuant to the requirements of the patent statutes, the principle of this invention has been explained and exemplified in a manner so that it can be readily practiced by those skilled in the art, such exemplification including what is considered to represent the best embodiment of the invention. However, it should be clearly understood that, within the scope of the appended claims, the invention may be practiced by those skilled in the art, and having the benefit of this disclosure, otherwise than as specifically described and exemplified herein.

What is claimed is:

1. A method of superbleaching a primary-bleached chemical or semichemical wood pulp, comprising treating the pulp in aqueous system with hydrogen peroxide in an amount of 0.01 to 0.5% by weight and N-benzoyl succinimide in the amount of 0.01 to 3% by weight, based on the dry weight of said pulp, at a pulp consistency of 2 to 85% by weight and at a pH of 2.5 to 9.5, the temperature of the treatment being 75° to 212° F. and the time of the treatment being 15 minutes to 16 hours, to provide a super-bleached pulp.

2. The method of claim 1 in which the hydrogen peroxide is present in the amount of 0.03 to 0.25% by weight based on the dry weight of the pulp.

3. The method of claim 1 in which the N-benzoyl succinimide is present in the amount of 0.1 to 1.0% by

weight based on the dry weight of the pulp.

4. The method of claim 1 in which the pulp consistency is 6 to 25% by weight.

5. The method of claim 1 in which the treatment is carried out at a pH of 6 to 8.

6. The method of claim 1 in which the temperature at which the treatment is carried out is 120° to 160° F.

7. The method of claim 1 in which the treatment is carried out for a time of 2 to 4 hours.

8. The method of claim 1 in which the hydrogen peroxide is present in the amount of 0.03 to 0.25% by weight

based on the dry weight of the pulp, the N-benzoyl succinimide is present in the amount of 0.1 to 1.0% by weight based on the weight of the pulp, the pH is 6 to 8, the pulp consistency is 6 to 25% by weight, the temperature is 120° to 160° F. and the treatment is carried out for 2 to 4 hours.

9. The method of claim 1 in which a molecularly dehydrated phosphate is present in an amount up to 1% by weight based on the dry weight of the pulp.

10. The method of claim 9 in which the molecularly dehydrated phosphate is present in the amount of 0.25 to 0.5% by weight based on the dry weight of the pulp.

11. The method of claim 1 in which sodium carbonate or sodium hydroxide is employed in an amount up to 0.5% by weight based on the dry weight of the pulp.

12. The method of claim 1 in which sodium carbonate or sodium hydroxide is employed in the amount of 0.1 to 0.25% by weight based on the weight of the dry pulp.

## References Cited

## UNITED STATES PATENTS

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HOWARD R. CAINE, Primary Examiner

U.S. Cl. X.R.

8—111; 162—78; 252—186

**UNITED STATES PATENT OFFICE**  
**CERTIFICATE OF CORRECTION**

Patent No. 3,462,344

Dated August 19, 1969

Inventor(s) Robert R. Kindron and George W. Houg

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 29, "designated" should read --designed--.

Column 3, line 24, "a caustic extraction" should be omitted.

Column 3, line 25, after "bleach;" the following was omitted  
--a sequence embodying a chlorine treatment, a caustic extraction, a hypochlorite bleach, a chlorine dioxide bleach, a caustic extraction and a chlorine dioxide bleach;--.

Column 5, line 13, Table 2, "0.3 sodium silicate" should read --3.0 sodium silicate--.

Column 5, line 52, "interefere" should read --interfere--.

Column 5, line 75, Claim 1, "super-bleached" should read --superbleached--.

**SIGNED AND  
SEALED**

**SEP 29 1970**

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**Attest:**

**Edward M. Fletcher, Jr.**  
**Attesting Officer**

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**Commissioner of Patents**