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3,687,803

ACID CHLORIDE ACTIVATORS FOR HYDROGEN PEROXIDE BLEACHING

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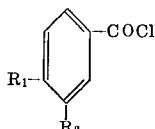
12 Claims

ABSTRACT OF THE DISCLOSURE

An oxygen bleaching composition comprising an oxygen bleach, such as hydrogen peroxide, and an activator, such as benzoyl chloride, useful in the bleaching of textiles and fibrous cellulosic materials such as wood pulp and straw. An improved process for the oxygen bleaching of textiles and wood pulp is also described.

Generally stated, the subject matter of the present invention relates to oxygen bleaching compositions for use in the textile and wood pulp industries.

More particularly, this invention relates to peroxide releasing compositions containing a benzoyl chloride activator having the formula:



wherein R_1 =hydrogen, halogen, nitro or lower alkoxy; and R_2 =hydrogen or halogen, with the proviso that when R_2 is halogen, R_1 must be hydrogen. These compounds have been found useful in possessing superior bleaching properties as well as having distinct economic advantages when used in the bleaching of wood pulp.

Still more particularly, this invention is related to a process for the bleaching of textiles or wood pulp in producing finished articles having a satisfactory appearance in quality and which resist "yellowing." "Yellowing" is that characteristic of a bleached finished product to continue oxidation at its various color centers on standing to form an off-white to yellow color of diminished brightness.

Compositions previously used in the bleaching of textile material or paper have frequently been of the chlorine type, such as sodium hypochlorite; or have utilized oxidizing gases such as chlorine, chlorine dioxide and sulfur dioxide. Liquid chlorine bleaches are generally unstable and lose their effective bleaching power upon prolonged storage. Such bleaches are difficult to handle and are actually destructive to the fabrics during the bleaching process. The disadvantages concomitant with the use of oxidizing gases are self evident. Both chlorine and chlorine dioxides are highly toxic and irritating to the eyes, nose and throat, and great care must be taken in the protection of all who work with these gases.

The primary object of bleaching cellulose textiles such as cotton fabrics is to remove color-causing non-cellulosic impurities, particularly cotton wax, in order to provide a fiber which is white, and which will take a dye uniformly when so treated. Due to the shortcomings of both the liquid chlorine bleaches and the oxidizing gases enumerated above as well as to the rising consumer dependence for fabrics which are sensitive to those more damaging bleaches, the use of oxygen bleaches has become increasingly of interest. Such oxygen bleaches generally comprise hydrogen peroxide, sodium peroxide, organic releasing peroxides such as urea peroxide, inorganic persalts such as sodium and potassium monoper-

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sulfate, and alkali metal perborates such as sodium and potassium perborate.

Oxygen bleaches are less harmful to textile fabrics and much safer to use. Sodium perborate and potassium monopersulfate are two of the most prominent choices of oxygen bleaches currently in use. They can be used in the form of a dry powder or tablet thus eliminating the inconvenience of adding a corrosive liquid or gas. The compositions of the present invention are such that they may be prepared and dispensed as aqueous solutions or added to solid carriers and dispensed as solid powders, flakes, granules or tablets.

In bleaching ligneous cellulosic materials such as wood pulp, the primary object is the oxidation of non-cellulosic material and the delignification and bleaching of lignin chromophores in order to produce a bleached groundwood or kraft pulp having a suitable brightness. Groundwood pulp now comprises 25% of the total annual production of pulp of which the newsprint industry consumes a major part. Normal delignification bleaching sequences in the manufacture of high brightness pulps frequently require additional bleaching steps depending upon pulp quality, consistency and reaction conditions in order to obtain a pulp having the necessary degree of brightness. Hence, it may be necessary to submit some wood pulps to a preliminary bleaching treatment with an alkali metal hypochlorite, such as sodium hypochlorite, followed by an oxidizing agent such as hydrogen peroxide, in order to produce the desired final degree of whiteness. Such a delignification process causes a substantial reduction in yield and adds considerably to production costs in order to obtain the higher brightness levels required for quality paper products. The present compositions and processes permit the preparation and use of groundwood pulp in a single bleaching operation for the preparation of such products as newsprint, cardboard, publication and specialty papers and so forth.

Many attempts have been made in the past to formulate oxygen bleaching compositions that will provide a safer and more convenient method of bleaching. Various activators have been added which promote or accelerate the bleaching action of such compositions, at the same time permitting the use of lower temperatures while still achieving the same degree of whiteness and spot removal.

Prior activators for oxygen bleaches include, for example, tris-(acetyl) cyanurate and tetraacetyl methylenediamine, as well as other hydrazine derivatives as disclosed in British Pat. No. 1,046,251, issued to Deutsche Gold-Und Silber-Scheideanstalt Vormals Roessler. Similarly U.S. 3,338,839 and U.S. 3,379,493 teach the use of mixed carboxylic acid anhydrides and acylated phosphonic acid esters or acylated phosphinic acid esters, respectively, as activators for peroxide bleaching compounds.

Most of the oxygen bleaches containing these activators have not proven entirely satisfactory, because of their high cost, and because they hydrolyze rapidly on storage or in aqueous alkaline media. Furthermore, they do not achieve a bleaching effectiveness comparable to that of liquid chlorine bleaches at water temperatures of about 50 to 70° C.

Accordingly, it is an object of the present invention to provide for an improved oxygen bleaching composition which effectively and economically bleaches at low temperatures.

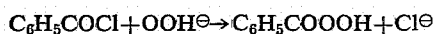
Another object of this invention is to provide for new and improved oxygen bleaching compositions which contain a hydrogen peroxide releasing organic peroxide or an inorganic persalt and a benzoyl chloride activator.

It is another object of this invention to provide compositions which will bleach textiles and cellulosic mate-

rial, notably wood pulp, by contacting a hydrogen peroxide releasing compound in alkaline solution under conditions of temperature and time such that effective bleaching occurs.

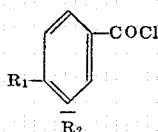
Additional objects and advantages will be apparent from the following description or taught by the practice of the invention as exemplified and as particularly pointed out in the appended claims.

The addition of benzoyl chloride to an oxygen bleach results in the in situ generation of perbenzoic acid according to the following reaction sequence:



It might have been presumed that a large number of acylating or alkylating groups would theoretically undergo a nucleophilic attack by the peroxide anion to yield an in situ peracid. However, few such compounds are competitive with the hydrolysis reaction of benzoyl chloride to benzoic acid, while at the same time possessing sufficient water solubility to be effective.

Compounds which have been found to be useful as activators in oxygen bleaching compositions are represented by the formula:



wherein R_1 =hydrogen, halogen, nitro or lower alkoxy; and R_2 =hydrogen or halogen, with the proviso that when R_2 is halogen, R_1 must be hydrogen.

Oxygen bleaches suitable for use with the activators of the present invention include, for example, hydrogen peroxide, sodium peroxide, organic releasing peroxides, such as urea peroxide, inorganic persalts, such as sodium and potassium monopersulfate, and alkali metal perborates such as sodium and potassium perborate, and the like. The preferred oxygen bleaching agents are hydrogen peroxide and sodium perborate due to their ready acceptance by the textile and wood pulp.

The quantity of activator used is generally sufficient so as to have one mole of activator present for each mole of available oxygen, that is a stoichiometric amount, although effective bleaching occurs at a lesser amount. It is preferred to use slightly larger than stoichiometric amounts to assure complete activation of the oxygen bleach. On the other hand lesser amounts of activator may be employed when a controlled bleaching effect is desired.

The activator/oxygen bleach compositions are employed in amounts sufficient to achieve the desired degree of bleaching. For home bleaching of textiles, amounts sufficient to supply 10 to 100 p.p.m. of active oxygen in the wash solution are normally employed. Commercial laundries and bleacheries may use as high as 200 p.p.m. in the wash solution. A preferred range for home bleaching is 25-75 p.p.m.

In practicing the present invention the activator/oxygen bleach compositions may be mixed with phosphate or other conventional detergent builders, such as sodium tripolyphosphate or nitrilotriacetate alone or in combination with other anionic, nonionic or cationic surfactants. These may include stabilizers, brighteners, and anti-redeposition agents such as sodium carboxymethylcellulose, all as well known in the art.

In the bleaching of groundwood pulp, where economics plays such an important role, the activator/oxygen bleach compositions are generally employed in amounts ranging from 0.1 to about 5.0% by weight based on O.D. (oven dried) pulp (calculated as equivalents of hydrogen peroxide with the appropriate molar amount of activator added). The preferred oxygen bleach compositions comprise a mixture of hydrogen peroxide and benzoyl chlo-

ride and are optimally used in 0.5-1.5% concentrations of the hydrogen peroxide portion for a pulp consistency of 5-25%.

One of the principal advantages to the present invention is the application in very alkaline solutions. Ordinarily it might be expected that an acid chloride would be rapidly hydrolyzed in an aqueous alkaline medium and be ineffective in forming a peracid from the peroxide present. However, as illustrated below the substituted benzoyl chloride activators of the present invention have a maximum efficiency over a wide alkaline range which makes them particularly useful in the textile and wood pulp bleaching industries.

In some instances difficulties occur in the use of oxygen bleaching since relatively high temperatures must be employed if the desired bleaching action is to be achieved. As a rule, temperatures almost up to the boiling temperature of water are used for washing or bleaching. Such high temperatures require a considerable expenditure of heat energy and are ill suited for the ordinary home washing machine. Furthermore, the use of such high temperatures results in substantial fabric degradation. The present textile oxygen bleach compositions are designed to be used at relatively low water temperatures of from about 50 to 70° C., such as those encountered in modern washing machines.

The bleaching of groundwood pulp is more effective at higher temperatures. However, the higher temperatures also result in a concomitant decrease in yield. Because of the very large quantities of water which must be heated, the economics of bleaching groundwood pulp at the maximum yield and at the minimum cost is a compromise between these two opposing effects. In general, a temperature range of from 35° C. to about 95° C. has been found to be effective with a temperature of 50° C. being preferred.

Another advantage of the present oxygen bleach compositions is that the presence of an activator enables the oxygen bleach to be utilized not only more effectively but to be utilized more rapidly. As can be seen from the appended data, the effect of contact time upon bleaching efficiency of groundwood pulp is of little or no importance and is not deemed to be critical in the practice of the present invention.

To more particularly point to the inventive features, reference is made to the following tables and examples. These examples illustrate the preparation of the activator/bleach compositions of the present invention as well as their use in the bleaching of textiles and groundwood pulp. These examples are merely illustrative and are not to be understood as limiting the scope or the underlying principles of the invention in anyway. All parts and percentages referred herein by weight unless otherwise indicated.

EXAMPLE 1

Standard Terg-O-Tometer test for bleach evaluation—tea stain

In order to evaluate the ability of the compositions of the present invention to effectively bleach textiles, a tea stain removal test was standardized as follows.

Five tea bags were added to one liter of boiling tap water and boiled for five minutes. Thirty-two desized white Indianhead Cotton cloth swatches (5" x 5") were then added and boiled for five minutes. The swatches were wrung out, dried at a high temperature, rinsed in cold water and again dried. The swatches so prepared were used within two weeks of their preparation.

In order to simulate home laundry conditions two stained cotton swatches were added to a stainless steel Terg-O-Tometer tumbler containing 1,000 ml. of a standard 0.15% detergent solution. Additional white terry cloth toweling was added to provide an average household wash water to cloth ratio of 20:1. Accurately measured quantities of activator and bleach were added along with a pre-

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determined quantity of sodium carbonate or sulfuric acid in order to obtain the desired pH and the whole solution was maintained at 50° C. The Terg-O-Tometer was then run at 100 cycles per minute for 15 minutes. The swatches were removed at the end of the wash cycle, rinsed under cold running water and ironed dry. Tests were run in duplicate with the experiments randomized.

Detergent blanks were run and reflectance readings taken both before and after the wash cycle using a standard Hunter Model D-40 Reflectometer and a blue filter. The swatches were read twice, on each side, both warp and fill, suitably backed with three similarly stained swatches. The fluorescent effect was excluded in all readings. The reflectance readings were averaged and the increase in reflectance of the stained swatch after washing was computed in accordance with the Kubelka-Munk equation:

Total percent stain removal= $\frac{R_3-R_4}{R_1-R_2} \times 100$

where
R₁=Reflectance unstained
R₂=Reflectance stained
R₃=Reflectance after bleaching
R₄=Reflectance stained

Table I shows the results obtained using activators with sodium perborate bleach, in an amount to provide 50 p.p.m. active oxygen.

TABLE I

pH	Activator	Activator/ perborate	Percent stain removal
10	Benzoyl chloride	1.0	64.0
10	p-Nitro benzoyl chloride	1.0	40.3
10	p-Methoxy benzoyl chloride	1.0	27.3
10	p-Chloro benzoyl chloride	1.0	64.4

Table II shows the results obtained for various ratios of activator to perborate compositions at different pH levels.

TABLE II

pH	Activator	Activator/ perborate	Percent stain removal
9	Benzoyl chloride	0.5	69.9
11	do	0.5	75.7
9	do	1.0	67.0
11	do	1.0	67.9
9	do	2.0	76.6
11	do	2.0	86.5

Table III shows the excellent results obtained over a wide range of alkaline pH levels.

EXAMPLE 2

Standardized determination of brightness for bleach evaluation of groundwood pulp

In order to demonstrate the effectiveness of the present compositions in the bleaching of wood pulp, a series of experiments were conducted under various conditions of pulp bleaching. Those bleaching experiments at 10% pulp consistency were done in the manner described by Wasser ST., vol. 15, 1819 (1969). The pulp slurry, generally containing 24.0 grams of O.D. (oven dried) pulp, was placed in a polyethylene bag. MgSO₄ (0.1% by weight of fiber) and Na₂SiO₃ (0.6% by weight of fiber) were added as stabilizers to prevent the decomposition of peroxide, and the pH adjusted to the desired alkalinity. The bags were immersed in a water bath to equilibrate at the temperature desired and the particular bleaching agent was added. The bags were occasionally removed to mix the contents by kneading the resultant slurry. Sodium bisulfite was added at the completion of the experiment to quench the oxidation. For the 2% consistency runs, stainless steel beakers were used which could be placed in a constant temperature bath.

Standard Noble-Wood hand sheet machines were used

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to convert the pulp to 8" x 8" sheets, which were then measured for their brightness. Brightness was measured using a General Electric Spectrophotometer which measured reflectance at 457 millimicrons (TAPPI Standard).

Table IV shows both the enhanced bleaching effect and the enhanced bleaching efficiency at various pulp consistencies in the use of an activator as compared to conventional bleaching using peroxide alone. As can be seen, acceptable brightness levels are achieved at 10-15% consistencies in considerably less than the normal 2 hour bleaching cycle. Results are given in G.E. Brightness Units.

TABLE IV
Pulp Consistencies

Bleaching agent	pH	Time	1%	2%	5%	10%	15%
1% H ₂ O ₂	10.5	2 hrs.	64.3	65.3	66.6	68.6	69.6
1% H ₂ O ₂ plus equiv. meta-chlorobenzoyl chloride.	8.5	15 mins.	62.9	71.1	69.7	69.3	67.7

TABLE V

Bleaching agent	pH	Consistency, percent	15 mins.	45 mins.	2 hrs.
1% H ₂ O ₂	10.5	10	61.2	61.5	62.8
1% H ₂ O ₂ plus equiv. of meta-chlorobenzoyl chloride.	10.5	2	67.3	66.2	64.3

Table VI shows the excellent and consistent results obtained over a wide range of alkaline pH levels when using a 1% meta-chlorobenzoyl chloride activator with an equivalent amount of hydrogen peroxide upon a 2% pulp consistency. In each case the bleaching time was 15 minutes.

TABLE VI

Initial pH	Final pH	Brightness
7.5	7.3	63.0
8.0	7.7	63.8
8.5	8.0	64.2
9.0	8.1	65.3
9.5	8.1	64.9
10.5	8.2	64.2

Table VII shows the effect of increasing quantities of bleach compositions comprising benzoyl chloride as activator and hydrogen peroxide as the oxygen bleach. The data was obtained after 15 minutes of bleaching of a 2% pulp consistency at a pH of 8.5.

TABLE VII

Percent peroxide/equiv. benzoyl chloride:	Brightness
0.20	63.5
0.30	64.6
0.40	65.6
0.50	66.4
0.60	67.2
0.70	67.7
0.80	68.3
0.90	69.0

Table VIII illustrates the effect of various ratios of activator to bleach. All pup slurries were bleached for 2 hours at a 2% consistency containing 1% hydrogen peroxide, and were buffered with a silicate buffer at pH 10.5.

TABLE VIII

Compositions (containing 1% H ₂ O ₂):	Brightness
No benzoyl chloride	66.6
0.3 equiv. benzoyl chloride	67.8
0.4 equiv. benzoyl chloride	68.3
0.5 equiv. benzoyl chloride	67.8
0.6 equiv. benzoyl chloride	68.4
0.7 equiv. benzoyl chloride	69.4
m-Chloro benzoyl chloride equiv. to peroxide	72.8

TABLE IX

Compositions (percent H ₂ O ₂ plus equiv. benzoyl chloride)	Brightness (40° C.)	Brightness (50° C.)
0.4-----	63.3	66.4
0.5-----	65.6	68.2
0.6-----	65.7	86.0
0.7-----	65.4	67.6
0.8-----	61.1	68.3
0.9-----	58.9	69.0

Table X shows the effect of equivalent treatment of various samples of pulp.

TABLE X

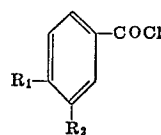
	Level in equiv. of H ₂ O ₂	Southern pine	Spruce poplar	Black spruce
H ₂ O ₂ at 10% consistency, pH=10.5, 2 hours.	0.00 -----		64.0	58.8
	0.25 -----		68.9	68.1
	0.50 -----	64.8	70.5	66.6
	0.75 -----	66.5	72.5	69.3
	1.00 -----	68.0	74.3	70.9
	1.50 -----	70.1	75.9	72.6
	2.00 -----		76.8	74.3
H ₂ O ₂ plus equiv. C ₆ H ₅ COCl, pH=10.5, 8.5, 15 min., 2% consistency.	0.25 -----	64.3	66.9	62.1
	0.50 -----	66.4	67.5	64.5
	0.75 -----	68.0		65.8
	1.00 -----	69.3	69.2	65.9
	1.50 -----		68.9	67.0
	2.00 -----			66.8
Meta chloroperbenzoic acid, pH=8.5, 15 min., 2% consistency.	0.25 -----	65.0	65.3	-----
	0.50 -----	68.0	67.8	63.5
	0.75 -----	70.1	-----	-----
	1.00 -----	71.4	70.3	65.3
	1.50 -----	-----	-----	66.4
	2.00 -----	-----	-----	-----

NOTE.—Southern pine—Samples 1-2 years old; stored in dry sheets. I.P. spruce-poplar—Fresh slurry from Hudson, N.Y. mill. Hawksbury black spruce—Solid material stored 3 months at 5° C.

I claim:

1. A bleaching composition comprising an oxygen bleaching agent, selected from the group consisting of hydrogen peroxide, alkali metal peroxides, organic peroxides,

inorganic persalts and alkali metal perborates, and an activator having the formula:



wherein R₁ is a member of the group consisting of hydrogen, halogen, nitro and lower alkoxy, and R₂ can be hydrogen and halogen, with the proviso that when R₂ is halogen, R₁ must be hydrogen.

2. The bleaching composition of claim 1 wherein the oxygen bleaching agent is hydrogen peroxide.

3. The bleaching composition of claim 2 wherein the oxygen bleaching agent is sodium perborate.

4. The bleaching composition of claim 1 wherein R₁ and R₂ are hydrogen.

5. The bleaching composition of claim 4 wherein R₁ is hydrogen and R₂ is chlorine.

6. The bleaching composition of claim 1 wherein the amount of oxygen bleaching agent used provides from 10 to 200 p.p.m. of active oxygen.

7. The bleaching composition of claim 6 wherein the amount of activator is about the stoichiometric equivalent of the available oxygen.

8. A process for bleaching cellulosic materials by treating with the composition of claim 1.

9. The process of claim 8 wherein the temperature of treatment is from about 35° to 95° C.

10. The process of claim 8 wherein the material treated is a cellulosic containing textile.

11. The process of claim 8 wherein the material treated is wood pulp.

12. The process of claim 8 wherein the material treated is paper pulp.

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HOWARD R. CAINE, Primary Examiner

U.S. Cl. X.R.

8—111; 162—78