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HYDROGEN PEROXIDE-AMMONIUM BICARBONATE ACIDIC BLEACHING COMPOSITION AND PROCESS

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This invention relates to the bleaching of various surfaces and to bleaching compositions which are especially well suited for such use.

Hydrogen peroxide solutions have heretofore been employed or proposed for bleaching various solid surfaces such as those of wood, paperboard, paper and floor covering products such as linoleum and rubber tiles. The use of strongly alkaline peroxide solutions have almost invariably been regarded as necessary for bleaching such surfaces. Solutions rendered alkaline by means of caustic soda, sodium silicate or other common non-volatile alkalies have been most widely used. Usually, bleaching is effected by drying, e.g. by heating, such a solution on the surface to be bleached. This leaves a bleached surface coated with an objectionable gritty residue of non-volatile alkali. Such residue can be removed by further processing at extra cost, e.g. by neutralization with an acid followed by washing. The use of ammonia as the alkaline agent has been proposed to avoid formation of such alkaline residue, but hydrogen peroxide solutions alkalized with ammonia do not give as effective bleaching as is generally desired.

It is an object of the invention to provide an improved peroxide method for bleaching such solid surfaces. A further object is to provide an improved peroxide method for bleaching such surfaces which avoids both the use of strongly alkaline peroxide solutions and the formation of solid residue when the bleach solution is dried on the solid surfaces being bleached. A particular object is to provide bleaching compositions which are especially well suited for use in practicing the improved method of the invention. Still further objects will be apparent from the following description.

The objects of the invention are accomplished by the formation of bleaching compositions which are aqueous solutions consisting essentially of hydrogen peroxide (H_2O_2) at a concentration in the range 10 to 50% and an ammonium carbonate at a concentration of at least 5% (both percentages being based upon the total weight of the composition), and by the use of such compositions in the bleaching of solid surfaces. Such surfaces can be readily and effectively bleached by subjecting the same to the action of such a composition. The solid surface can simply be wet or coated uniformly with the composition which is then dried on the surface either at ordinary or elevated temperatures.

Any of the ammonium carbonates can be used in practicing the invention. These include ammonium bicarbonate, NH_4HCO_3; ammonium sesquicarbonate, $2NH_4HCO_3 \cdot (NH_4)_2CO_3 \cdot H_2O$; ammonium carbonate, $(NH_4)_2CO_3 \cdot H_2O$; and the common "ammonium carbonate" of commerce, known also as "sal volatile" or "Hartshorn salt," generally regarded as a double salt or mixture of the bicarbonate and carbamate,

$$NH_4HCO_3 \cdot NH_2COONH_4$$

Mixtures of any two or more of these ammonium carbonate compounds can also be used. The preferred ammonium carbonate compound is the bicarbonate since its use gives bleaching compositions which are non-alkaline (pH about 6.6–6.9) and somewhat more stable than those obtained using ammonium carbonate.

The concentration of the ammonium carbonate or bicarbonate in the bleaching composition should be at least 5% by weight based upon the weight of the composition in order to obtain the rapid and effective bleaching generally desired. Higher concentrations up to the saturation concentration can be used, concentrations ranging from about 10 to 23% being generally preferred.

The concentration of hydrogen peroxide (H_2O_2) in the bleaching composition generally should be at least 10% of the weight of the composition. Higher concentrations, e.g., up to about 50% are suitable and those in the range 20 to 40% are generally preferred because of their rapid effective bleaching action, particularly when they also contain an ammonium carbonate at a concentration in the preferred range. The present compositions are readily prepared simply by dissolving the required amount of the ammonium carbonate compound in a commercial aqueous hydrogen peroxide, e.g., of about 27 to 50% strength. No cooling is required during their preparation to prevent peroxide decomposition. This is particularly so when making the preferred peroxide-bicarbonate compositions, since ammonium bicarbonate dissolves in aqueous hyrogen peroxide with a negative heat of solution.

Aqueous bleaching compositions of the above type free of reagents other than hydrogen peroxide and the ammonium carbonate compound are highly effective for the present purpose and are generally preferred. They are substantially neutral in reaction, e.g. the pH of the peroxide-carbonate compositions will range from about 7.6 to 7.9 and the pH of the peroxide-bicarbonate compositions will range from about 6.6 to 6.9. However, since such compositions tend to decompose upon long standing, it may be desirable in instances where they are to be prepared considerably in advance of their use to add to the composition a small amount of peroxide stabilizer. Any of the known peroxide stabilizers can be used, particularly when they are employed in small amounts as will generally be the case. The preferred stabilizers are compounds which when used in small amounts will not increase significantly the alkalinity of the composition. Illustrative of these are ammonium acetate, ammonium dihydrogen phosphate and citric acid, which are effective stabilizers at concentrations of about 0.5 to 1.0% in the composition. In some instances, it may also be advantageous to add to the composition a small amount of a wetting agent to improve the wetting property of the composition.

Any of the solid surfaces heretofore known to respond to bleaching with hydrogen peroxide can in general be bleached by means of the present compositions. Illustrative are the surfaces of wood and wooden articles, paperboard, paper, fiber based acoustical tile such as wood pulp and bagasse tiles, and floor coverings such as linoleum and rubber tile. These floor covering products are generally prepared from compositions which contain unsaturated materials such as drying oils or rubber which give surfaces with a yellowish discoloration during the usual heat curing operation in the manufacture of such products. Such surfaces can be rapidly and effectively bleached simply by wetting or coating them uniformly with the present bleaching composition and permitting the wet surface to dry at ordinary or elevated temperatures.

The invention is illustrated by the following examples in which all percentages and parts of reagents are by weight.

Example 1

Two solutions were prepared as follows:

A. One part of solid ammonium carbonate,

$$(NH_4)_2CO_3 \cdot H_2O$$

(30% NH_3 equivalent), was dissolved in 9 parts of 35% aqueous hydrogen peroxide. The resulting solution had a pH of 7.75.

B. One part of 28% aqueous ammonia was added to 9 parts of 35% aqueous hydrogen peroxide. The resulting solution had a pH of 8.75.

The surfaces of samples of an unbleached kraft paperboard were sprayed uniformly with one or the other of the above solutions at an application rate of 3 lbs. of solution per 1000 sq. ft. of board surface. Immediately after spraying, the sprayed surface was contacted for about 5 seconds with a smooth aluminum surface previously heated to a temperature of 325 to 350° F., whereby the surface was rapidly dried and bleached. Although uniform bleaching resulted in each instance, the degree of bleaching was much greater when Solution A was used. The brightness (percent reflectance of blue light) of the samples as measured by a Hunter Multipurpose Reflectometer was 15 for the unbleached board, 29 for the board bleached with Solution A and 24 for the board bleached with Solution B.

In similar trials it was found that other ammonium salts such as the acetate, the citrate and mono- and diammonium phosphates, when used in place of ammonium carbonate in Solution A, gave distinctly poorer bleaching results in that bleaching was much less and uneven and the dried bleached surfaces were gritty due to residual salt.

Example 2

A bleaching solution prepared by dissolving 1 part of ammonium bicarbonate (NH_4HCO_3) in 4 parts of 35% aqueous hydrogen peroxide was applied uniformly at a rate of 8 lbs. per 1000 sq. ft. to a paperboard having a surface layer of semi-bleached kraft pulp. The surface with the applied solution was heated and dried by contact for 10 seconds with a smooth metal surface preheated to a temperature of 325° F. The treatment increased the brightness of the board from 54 to 67.

Example 3

A bleaching solution prepared by dissolving 1 part of ammonium bicarbonate in 4 parts of 50% aqueous hydrogen peroxide was applied with a roller applicator to the surface of a rubber floor tile at a rate of about 6 lbs. per 1000 sq. ft. The tile composition was about 17% GRS rubber (butadiene-styrene copolymer), 10% silica, 30% clay, 20% whiting and asbestine, and 23% pigment. Prior to application of the bleaching solution, the tile surface was wet with a 50% solution of C-cetyl betaine, a wetting agent. The tile surface with the applied bleaching solution was dried and bleached by contacting it for a few seconds with a smooth chromium plated metal surface preheated to 300° F.

The tile originally had a mottled white and black surface, the white portions having a definite yellowish shade. After the above treatment, the black portions were unchanged but the yellowness had been removed from the white portions. This bleaching solution left no solid residue on either the tile or the metal surface used for heating, and caused no significant roughening of the tile surface. When similar bleaching solutions containing alkalies such as caustic soda and sodium silicate are used in place of the above solution, they tend to give a roughened tile surface and leave an objectionable residue both on the tile and the metal surface used for heating.

Example 4

A rubber floor tile of the composition given in Example 3 was treated substantially as described in that example except that the bleaching solution was prepared by dissolving 1 part of ammonium bicarbonate in 9 parts of 50% aqueous hydrogen peroxide and the tile with the applied solution was heated by being placed for 5 minutes in an oven maintained at 220° F. The original yellowish white portions of the tile were converted to a clear white and no roughening of the tile surface resulted.

Linoleum, which generally has a yellowish discoloration resulting from heat curing during manufacture, can be bleached by the method of Examples 3 and 4.

Example 5

Three bleaching solutions were prepared as follows:

A. One part of ammonium carbonate was dissolved in 9 parts of 35% aqueous hydrogen peroxide.

B. One part of ammonium carbonate was dissolved in 4 parts of 35% aqueous hydrogen peroxide.

C. A solution was prepared by adding 20 parts of caustic soda, 1 part of 42° Bé. aqueous sodium silicate and 1 part of calcium oxide, to 130 parts of water. One part of the resulting solution was then added to 3 parts of 35% aqueous hydrogen peroxide to give the bleaching solution.

Each of Solutions A, B, and C was sprayed onto separate marked portions of the vertical surface of a solid block of walnut wood. As much of each solution was sprayed on as would remain on the vertical surface. After spraying, the block was allowed to dry 30 minutes at room temperature and then was heated at 130° F. for 15 minutes. The surfaces treated with Solutions B and C were bleached to about the same degree while that treated with Solution A was bleached slightly less. The surface treated with Solution C was covered with a gritty alkaline residue and contained a large amount of residual peroxide. The surfaces bleached with Solutions A and B were slightly acidic and contained only small amounts of residual peroxide. Since the successful application of a finish to a bleached wood surface requires that the surface be non-alkaline, e.g., neutral or slightly acidic, and substantially free of residual peroxide, Solutions A and B are distinctly advantageous over Solution C for use in bleaching wood in preparation for finishing with the usual stains, varnishes and lacquers.

Example 6

The following bleach solutions were prepared by mixing the components indicated in the proportions shown:

Component	Solutions						
	A	B	C	D	E	F	G
35% aq. H_2O_2, parts	80	80	80	80	85	80	95
NH_4HCO_3, parts	20	15	10	----	----	----	5
$(NH_4)_2HPO_4$, parts	----	5	10	20	----	----	----
Sodium tripolyphosphate, parts	----	----	----	----	10	----	----
Borax, parts	----	----	----	----	4	----	----
Sequestering agent,[1] parts	----	----	----	----	1	----	----
Water, parts	----	----	----	----	----	20	----

[1] A commercial sodium salt of ethylene diamine tetra-acetic acid.

The above solutions were brushed onto the surfaces of samples of a wood pulp accoustical tile at the application rates indicated in the following Table of Results. The samples were then dried in a circulating hot air oven for 3 to 5 minutes at a temperature of 105 to 120° F. The untreated tiles had a brightness of 32.4. The brightnesses of the treated samples are shown below.

TABLE OF RESULTS

Solution	Application Rate, Grams/Sq. Ft.	Sample Brightness	Brightness Increase, Points
A	3.8	57.8	25.8
B	4.2	56.0	23.6
C	3.8	52.1	19.7
D	3.7	41.5	9.1
E	4.17	39.0	6.6
F	5.8	47.3	14.9
G	4.4	56.0	23.6

The sample using Solution F did not attain maximum brightness until several hours after removal from the

oven. In all other instances, maximum brightness was reached during drying in the oven.

A comparison of the results for Solutions A, B, C and G with those for Solution F shows that the presence of ammonium bicarbonate in the bleach solution very markedly increases bleaching. The results for Solution E show that sodium tripolyphosphate and borax are not a satisfactory substitute for ammonium bicarbonate. The results for Solutions A, B, C and D show clearly that the brightness obtained decreases markedly and progressively as ammonium bicrabonate is progressively replaced by diammonium phosphate. However, the addition of an ammonium phosphate to the bleach formula imparts flame resistant properties to the bleached tile, so that it will be advantageous in instances where it is desired to bleach and impart flameproofing properties simultaneously to include some ammonium phosphate compound along with the ammonium carbonate compound in the bleaching composition.

Example 7

Bagasse acoustical tile samples were successfully bleached by the general method of Example 6 using bleaching Solution A of that example. In several trials the brightness was increased from about 47 to 62 employing Solution A at full strength and at dilutions of 1:1 and 1:2. Similar results were also obtained when the tile samples with the applied solution were dried at room temperature.

Example 8

A bleaching solution was prepared by dissolving 1 part of ammonium bicarbonate in 9 parts of 35% aqueous hydrogen peroxide. The solution was applied uniformly to the surface of a kraft paper at the rate of 3 lbs. per 1000 sq. ft. The paper surface with its applied solution was then immediately dried and bleached by contacting it for 10 seconds with a smooth metal surface preheated to 300° F. This treatment increased the surface brightness of the paper from 29.5 to 53.5. The surface brightness of a kraft paperboard was increased from 26.5 to 47.3 by a similar treatment.

The present bleaching compositions can be applied to the surface to be bleached by spraying, dipping, brushing or sponging methods, or by other conventional ways of applying solutions such as by the use of a roller applicator. The bleaching solution effectively bleaches at ordinary temperature, but it is generally preferred to employ higher temperatures such as may be obtained by the use of hot air or infrared radiation. Heating by directly contacting the surface coated with the bleaching solution with a smooth metal surface preheated to the desired temperature gives excellent results. Metal surfaces at temperatures of 300 to 400° F. have been successfully used, as have also hot-air ovens at temperatures up to about 700° F. Oven or metal surface temperatures should, of course, not be so high as to damage the surface being treated. Heating for a time sufficient to dry the bleaching solution on the surface is generally satisfactory and heating times of a few seconds at the higher temperatures up to 10 to 15 minutes at lower temperatures are generally suitable. Air drying over longer times at ordinary temperature can also be used.

The bleaching solution will contain as essential components at least 10% hydrogen peroxide (H_2O_2) and at least 5% ammonium carbonate compound. The hydrogen peroxide concentration may range up to about 50%, the preferred range being 20 to 40%. Concentrations of hydrogen peroxide below 10% and of the ammonium carbonate below 5% are usually too low to give the rapid bleaching desired. The preferred concentrations for the ammonium carbonate compound range from about 10 to 23% but higher concentrations up to saturation can be used.

As indicated previously, it may be desirable in some instances to add to the bleaching composition small amounts of a peroxide stabilizer, or of a wetting agent or of a flameproofing agent such as an ammonium phosphate. However, the presence of such other agents is not essential to the obtainment of good and rapid bleaching and aqueous solutions containing no other reagent than hydrogen peroxide and the chosen ammonium carbonate compound will generally be satisfactory for most purposes.

The present invention provides bleaching compositions which are especially well suited for bleaching solid surfaces of the type heretofore known to respond to bleaching with hydrogen peroxide. Bleaching of such surfaces can be effected rapidly and effectively by the present method to obtain directly bleached surfaces which are not roughened and are free of undesired residual materials.

I claim:

1. An aqueous acidic bleaching solution having a pH in the range of from 6.6 to 6.9 consisting essentially of water, 10–50% by weight hydrogen peroxide and 10–23% by weight ammonium bicarbonate.

2. The method of bleaching a solid surface comprising wetting said surface with an aqueous acidic bleaching solution having a pH in the range of from about 6.6 to 6.9 consisting essentially of water, 10–50% hydrogen peroxide and 10–23% by weight ammonium bicarbonate.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,034,851 May 15, 1962

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It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 6, line 30, after "from" insert -- about --.

Signed and sealed this 11th day of September 1962.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents