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METHOD FOR OXIDATIVELY TREATING FLOUR

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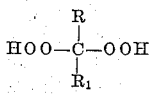
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8 Claims. (Cl. 99—232)

This invention relates to the oxidative treatment of cereal flours and, more particularly, to a method for oxidatively treating flour to bleach and/or mature the same.

Both maturing and bleaching of flours results from oxidative changes in the flour. Maturing can be considered as the same oxidative change which would result from natural aging of the flour for a prolonged period, while bleaching results from the more or less complete oxidation of the carotinoid pigments of the flour to colorless reaction products. In the past, numerous agents have been proposed for oxidatively treating flour. Of these prior-art agents, most have been useful to accomplish only maturing or only bleaching. Thus, the bromates, the iodates and the persulfates, all accepted maturing agents, have no bleaching power. Conversely, benzoyl peroxide, one of the commonly accepted bleaching agents has no maturing power. Prior art workers have long sought agents which would be acceptable for flour treatment and which would have the dual capability of both maturing and bleaching flours. Until recently, chlorine dioxide has been the only agent available to the trade which would both mature and bleach flour. Chlorine dioxide has, however, proved to be disadvantageous in several respects, the primary disadvantage being that it is too potent, so that an unduly critical control of the amount used must be maintained to avoid over-treatment and damage to color and baking quality of the flour.

More recently, the continuing search for other dual-function oxidative agents for treating flour has led to the discovery thta certain acyclic, monomeric dihydroperoxy compounds of the general formula

(1)



where R and R_1 are the same or different alkyl groups having 1–4 carbon atoms, are capable of both maturing and bleaching flour. For example, as disclosed in my copending application Serial No. 75,774, filed December 14, 1960, now Patent No. 3,077,412, issued February 12, 1963, 2,2-dihydroperoxy propane is an excellent flour maturing and bleaching agent. However, such compounds do not ordinarily occur in solid form and their introduction into flour accordingly presents some difficulty. For example, 2,2-dihydroperoxy propane is a very viscous liquid at room temperature and has, therefore, heretofore been introduced into flour either in the form of a liquid solution or supported on a suitable solid carrier material such as corn starch. While the use of such dihydroperoxy compounds, either in the form of a liquid solution or in a carrier-supported composition, is practical, the preparation of such compositions involves manufacturing difficulties and attendant losses in peroxide activity which it is desirable to avoid.

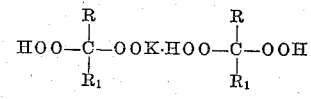
It has long been recognized by the trade, particularly in view of the long history of use of benzoyl peroxide, that the treatment of flour is greatly simplified and expedited if a solid, relatively stable treating agent can be employed. Accordingly, those skilled in the art have long sought to discover a treating agent which would have the effectiveness of compounds like 2,2-dihydroperoxy propane, for example, yet would be available in stable, solid form.

A general object of the present invention is to provide an improved method for oxidatively treating flour to at least mature the same.

Another object is to provide a method for oxidatively treating flour wherein the desired oxidative activity is introduced into the flour by the simple addition of a compound which is solid, stable for practical purposes and at least substantially odorless under the conditions of use.

In accordance with the present method, flour is bleached and/or matured by incorporating therein small but effective amounts of at least one normally solid, substantially odorless addition compound of the general formula

(2)



wherein R and R_1 are alkyl groups having 1–4 carbon atoms. Described and claimed per se in my copending application Serial No. 220,895, filed concurrently herewith, such compounds include

2-hydroperoxy-2-potassiumperoxy propane·2,2-dihydroperoxy propane
2-hydroperoxy-2-potassiumperoxy butane·2,2-dihydroperoxy butane
2-hydroperoxy-2-potassiumperoxy-3-methyl butane·2,2-dihydroperoxy-3-methyl butane
2-hydroperoxy-2-potassiumperoxy-4-methyl pentane·2,2-dihydroperoxy-4-methyl pentane
3-hydroperoxy-3-potassiumperoxy pentane·3,3-dihydroperoxy pentane

Though such compounds are solid at room temperature, are substantially odorless, and are adequately stable for use in the present method, they exhibit bleaching and maturing capabilities at least equal to the corresponding monomeric, dihydroperoxy compounds from which they are derived.

Additional compounds in accordance with Formula 2 can be prepared, as described in detail in the aforesaid copending application Serial No. 220,895, by reacting a potassium base with the appropriate monomeric dihydroperoxide in a liquid medium at or below room temperature. The addition compound precipitates promptly and is ordinarily recoverable in essentially pure form simply by separation of the precipitate from the mother liquor, followed by washing and drying of the recovered crystals.

In pure form, the addition compounds described above are dangerous, being autoexplosive and highly flammable. However, when blended with a suitable extender, such as corn starch, for example, such compounds are entirely safe for storage, handling and use with ordinary accepted procedures.

In practicing the present method in its most advantageous form, a solid, particulate composition comprising at least one addition compound in accordance with Formula 2 is intimately mixed with the flour to be treated in a small amount effective to carry into the flour a hydrogen peroxide equivalent content of from about 0.0005% to a few hundredths of a percent of the weight of the flour to be treated. The amount of the addition compound employed depends in part upon the nature of the flour being treated and in part upon the end result desired. Thus, with flours which are amenable to oxidative change, and when only maturing is desired, amounts of the addition compound yielding a hydrogen peroxide equivalent content as low as 0.0005% of the flour weight are adequate. Of course, with flours which are more difficult to treat, the amount of treating agent is increased even when only maturing is desired. With easily treated flours, such as the so-called "low extraction flours," bleaching can be accomplished with the addition agent being

added in amounts yielding hydrogen peroxide equivalent contents as low as 0.001% of the flour weight. In the case of "high extraction flours," containing more of the total wheat kernel, larger quantities of the addition compound are employed, a hydrogen peroxide equivalent content on the order of 0.006–0.012% of the flour weight ordinarily being satisfactory. With products which are distinctly more difficult to bleach, such as second clear flours, for example, bleaching and maturing can be accomplished with amounts of the addition compounds providing a hydrogen peroxide equivalent content up to 0.03% of the flour weight.

Solid, particulate, edible extenders suitable for use in accordance with the invention include food starches, heat-modified food starches, dextrines, cereal flours, defatted cereal flours, heat-treated cereal flours, pre-oxidized starches and flours, wheat gluten, the vegetable proteins, including particularly soybean protein, and edible inorganic compounds such as the inorganic phosphates and calcium sulfate, which are inert to peroxides.

In general, the extender or extenders must be employed in a quantity adequate to render the solid addition compound (Formula 2) stable for the purposes of the present method. Thus, the amount of the extender must be at least such that the weight ratio of the addition compound to the extender is not more than 3:1. Of course, as high a proportion of the extender or diluent can be employed as is desirable under the particular circumstances of use. The upper limit on the extender is set only by the economics of the method and, under most circumstances, the weight ratio of addition compound to diluent will not exceed 1:1000.

Though addition compounds in accordance with Formula 2 are flammable and explosive, their stability under normal conditions is such that they can be blended with solid, particulate diluents without unusual danger. For this purpose, most conventional blending devices can be employed and it is convenient to use the usual flour blenders.

When the addition compounds of this invention are blended with a particulate diluent or extender to form a free flowing composition which can be handled by the usual feeders employed in flour mills, the relative proportions of the solid addition compound and the diluent are so chosen that the mixture, when fed to the flour at a convenient rate for the miller, will introduce into the flour the desired hydrogen peroxide equivalent for bleaching of the particular flour at hand. It will thus be understood that the mixture of the addition compound and the diluent can be made such as to have any given hydrogen peroxide equivalent content such, for example, as 25% by weight.

The following examples are typical:

Example 1

A. *Preparation of 2-hydroperoxy-2-potassiumperoxy propane·2,2dihydroperoxy propane.*—57 parts by volume of aqueous hydrogen peroxide solution (50% H_2O_2 by weight) and 37 parts by volume of acetone are mixed and cooled to 0° C. The resulting reaction mixture is catalyzed by addition of 2 parts by volume of 1 N hydrochloric acid. Employing a crushed ice-salt water bath, the reaction mixture is kept at 0–10° C. for 60 min. The resulting reaction product mixture is then neutralized by addition of 2.3 parts by volume of 1 N sodium hydroxide. 10 parts by weight of the reaction product mixture so obtained is placed in an open vessel and 4 parts by weight of aqueous potassium hydroxide solution (50% KOH by weight) is added. The mixture is stirred continuously and maintained slightly below room temperature. A white, snowy precipitate forms within a few minutes, filling the entire vessel. The precipitate is separated from the mother liquor and washed with methanol. The recovered, washed crystals are then redissolved in water (10:1 water-to-solid) and cooled to recrystallize. The fresh crystals are recovered and washed, first with acetone and then with ether. *Analysis.*—(1) Calculated for 2-hydroperoxy-2-potassiumperoxy propane·2,2-dihydroperoxy propane: K=15.35%, active O_2=25.2%. (2) Found: K=15.30%, active O_2=25.2%.

B. *Preparation of bleaching and maturing compositions.*—Composition A was prepared by blending 25 g. of the pure 2-hydroperoxy-2-potassiumperoxy propane·2,2-dihydroperoxy propane in dry, crystalline form, as obtained in section A of this example, with 25 g. of dry, food grade corn starch, blending being accomplished in a conventional flour blender. Composition B was prepared by reacting acetone and hydrogen peroxide as described in section A of this example to provide a liquid reaction mixture containing 2,2-dihydroperoxy propane and acyclic polymers thereof, and then extracting the resulting reaction mixture with pentane to leave as an aqueous residue a substantially pure aqueous solution of 2,2-dihydroperoxy propane, this aqueous solution then being combined with food grade corn starch and dried to provide a free-flowing composition.

C. *Bleaching and maturing wheat flour.*—Equal quantities of the same unbleached, commercial, bread wheat flour (Liberty Special) were obtained. Composition A was blended with one such quantity of the flour, and composition B with the other, each additive composition providing a hydrogen peroxide equivalent content equal to 0.003% of the flour weight. The two lots of flour were separately agitated to assure uniform distribution of the treating agents therethrough and were then allowed to stand at room temperature, carotene contents being determined at the end of the third and seventh days, as follows:

	Carotene Content (p.p.m.)		Percent Carotene Removal
	3 Days	7 Days	
Control	2.11	2.14	----------
Composition A	1.33	1.23	41.7
Composition B	1.44	1.23	41.7

Both bleached quantities of flour were then used to bake bread in conventional fashion, the doughs being observed for indications that the flour was adequately matured. The dough characteristics were essentially the same for each treated lot of flour and indicated that good maturing had been accomplished in each case.

Employing compositions A and B of this example, the procedure was repeated with an unbleached second clear flour, the peroxidic compositions being used at levels providing a hydrogen peroxide equivalent content equal to 0.01% of the flour weight, the carotene determinations being as follows:

	Carotene Content (p.p.m.)		Percent Carotene Removal
	4 Days	7 Days	
Control	2.85	2.79	----------
Composition A	2.14	1.89	32.25
Composition B	2.30	1.97	29.39

Example 2

A. *Preparation of 2-hydroperoxy-2-potassiumperoxy butane·2,2-dihydroperoxy butane.*—114.0 parts by volume of aqueous hydrogen peroxide solution (50% H_2O_2 by weight), 89.5 parts by volume methyl ethyl ketone, and 2.0 parts by volume of aqueous sulfuric acid (20% H_2SO_4 by weight) were mixed in an open vessel and maintained for 1 hr. at 30° C. At the end of that period, 15.0 parts by volume of 1 N sodium hydroxide solution was added to neutralize the acid. The reaction mixture was agitated throughout the 1 hr. period to avoid phase sep-

aration during the reaction. After addition of the sodium hydroxide, 89.5 parts by volume of methyl ethyl ketone was added to promote phase separation and the liquid mixture was allowed to stand until distinct upper and lower phases formed. The lower layer was removed and the upper layer recovered and dried with anhydrous sodium sulfate. 50.0 parts by volume of the recovered material was combined at room temperature in an open vessel with 10.6 parts by volume of aqueous potassium hydroxide (50% KOH by weight). A voluminous white precipitate formed after approximately 30 sec. The precipitate was recovered, washed four times with ethanol and dried with ethyl ether. The recovered product was agitated in 30.0 parts by volume of distilled water and the resulting solution filtered to remove the undissolved portion. The clear solution was cooled to 5° C. and held at that temperature for several hours. The resulting crystallized material was recovered and washed twice with ethanol and twice with ethyl ether. *Analysis.*—(1) Calculated for 2-hydroperoxy-2-potassiumperoxy butane·2,2-dihydroperoxy butane: K=13.8%, active O_2=22.8%. (2) Found: K=13.5%, active O_2=22.6%.

B. *Preparation of bleaching and maturing composition.*—The purified, crystalline 2-hydroperoxy-2-potassiumperoxy butane·2,2-dihydroperoxy butane was blended with dry food grade corn starch to provide a free flowing composition wherein the addition compound gave a hydrogen peroxide equivalent content equal to 12.4% of the total weight of the composition. Preparation of the composition was accomplished by placing the corn starch in a laboratory scale flour blender, then introducing the addition compound, and then blending the mixture.

C. *Bleaching and maturing wheat flour.*—The composition prepared in section B of this example was combined with an unbleached, commercial, bread wheat flour, the amount of the composition used being such as to introduce into the flour a hydrogen peroxide equivalent content equal to 0.003% of the flour weight. After introduction of the treating composition, the flour was agitated in a flour blender to accomplish uniform distribution of the addition compound through the flour. The treated quantity of flour, and a like quantity of untreated flour as control, were maintained at room temperature for 67 hrs. and the carotene contents then determined. The control flour had a carotene content of 2.14 p.p.m., while the treated flour was found to have a carotene content of 1.47 p.p.m. The treated flour was then used to make bread in conventional fashion, the dough being observed for indications that the flour was properly matured. The dough was found to be excellent in all respects, showing that the addition compound had properly matured the flour.

Example 3

A. *Preparation of 3-hydroperoxy-3-potassiumperoxy pentane·3,3-dihydroperoxy pentane.*—43.0 parts by weight of diethyl ketone, 68.0 parts by weight of aqueous hydrogen peroxide solution (50% H_2O_2 by weight), and 1.0 part by weight of aqueous sulfuric acid (20% H_2SO_4 by weight) were mixed in an open vessel and maintained, with agitation, at 27–34° C. for 1 hr. At the end of that period, the reaction product mixture was allowed to stand at room temperature and separated into distinct upper and lower phases. The upper phase was recovered and dried with anhydrous sodium sulfate. 25.0 parts by volume of the recovered, dried material was combined at room temperature in an open vessel with an amount of aqueous potassium hydroxide solution (50% KOH by weight) providing 1 g. of the potassium hydroxide solution for each 3.33 ml. of the recovered reaction product. A voluminous white precipitate formed instantaneously and was recovered by vacuum filtration. The recovered precipitate was washed four times with ethanol and dried at room temperature. *Analysis without recrystallization.*—(1) Calculated for 3-hydroperoxy-3-potassiumperoxy pentane·3,3-dihydroperoxy pentane: K=12.6%, active O_2=20.7%. (2) Found: K=12.4%, active O_2=20.0%.

B. *Preparation of bleaching and maturing compositions.*—Composition A is prepared by blending equal parts by weight of the 3-hydroperoxy-3-potassiumperoxy pentane·3,3-dihydroperoxy pentane and dry, food grade corn starch. To prepare composition B, diethyl ketone and aqueous hydrogen peroxide were reacted in accordance with section A of this example, the upper layer of the resulting liquid reaction product mixture being recovered as a solution containing a major proportion of 3,3-dihydroperoxy pentane, as well as some polymeric acyclic dihydroperoxides of diethyl ketone. The recovered liquid material was blended with dry, food grade corn starch in an amount providing in the resulting composition, hereinafter referred to as composition B, a hydrogen peroxide equivalent content equal to that of composition A. It was observed that, while composition A was odorless, composition B exhibited a relatively strong ketone odor.

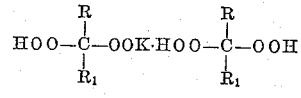
C. *Bleaching and maturing wheat flour.*—Compositions A and B of this example were separately combined with like quantities of the same commercial, unbleached bread wheat flour, the amounts of the two compositions employed being such as to introduce into each quantity of treated flour a hydrogen peroxide equivalent content equal to 0.003% by weight, based on the flour. At the end of three days, both quantities of flour exhibited marked color removal, indicating that both compositions A and B were effective to bleach the flour. The flour bleached with composition A was then employed to make bread in conventional fashion, the character of the dough being completely satisfactory and indicating that the flour had been adequately matured by composition A.

In general, all of the addition compounds in accordance with Formula 2 are capable of both bleaching and maturing flour at least to the same extent as are the corresponding monomeric dihydroperoxides. All of the addition compounds are substantially odorless and have the distinct advantage of not introducing ketone-like odors to the treated flour. Because obtainable in pure form, and because adequately stable when so obtained, the addition compounds allow production of dry, free-flowing treating compositions which contain a relatively high hydrogen peroxide equivalent content. This is a distinct advantage of the invention since, when employing the monomeric dihydroperoxides, such compounds must be distributed on a carrier material and the resulting composition dried to at least some extent, with attendant loss of active oxygen.

While particularly advantageous embodiments of the invention have been described, it will be understood by those skilled in the art that various changes and modifications can be made therein without departing from the scope of the invention as defined in the appended claims.

What is claimed is:

1. The method for oxidatively treating flour to at least mature the same, comprising incorporating in the flour a small but effective proportion of an addition compound of the general formula



where R and R_1 are alkyl radicals containing 1–4 carbon atoms, the quantity of said addition compound employed being such as to introduce into the flour a hydrogen peroxide equivalent content of from 0.0005% to a few hundredths of a percent of the flour weight.

2. The method of claim 1, wherein said addition compound is in solid, particulate form.

3. The method of claim 2, wherein said addition com-

pound is employed in admixture with a particulate starchy cereal extender.

4. The method for oxidatively treating flour to at least mature the same comprising mixing with the flour an amount of 2-hydroperoxy-2-potassiumperoxy propane·2,2-dihydroperoxy propane adequate to introduce into the flour a hydrogen peroxide equivalent content of from 0.0005% to a few hundredths of a percent of the flour weight.

5. The method for oxidatively treating flour to at least mature the same comprising mixing with the flour an amount of 2-hydroperoxy-2-potassiumperoxy butane·2,2-dihydroperoxy butane adequate to introduce into the flour a hydrogen peroxide equivalent content of from 0.0005% to a few hundredths of a percent of the flour weight.

6. The method for oxidatively treating flour to at least mature the same comprising mixing with the flour an amount of 2-hydroperoxy-2-potassiumperoxy-3-methyl butane·2,2-dihydroperoxy-3-methyl butane adequate to introduce into the flour a hydrogen peroxide equivalent

content of from 0.0005% to a few hundredths of a percent of the flour weight.

7. The method for oxidatively treating flour to at least mature the same comprising mixing with the flour an amount of 2-hydroperoxy-2-potassiumperoxy-4-methyl pentane·2,2-dihydroperoxy-4-methyl pentane adequate to introduce into the flour a hydrogen peroxide esuivalent content of from 0.0005% to a few hundredths of a percent of the flour weight.

8. The method for oxidatively treating flour to at least mature the same comprising mixing with the flour an amount of 3-hydroperoxy-3-potassiumperoxy pentane·3,3-dihydroperoxy pentane adequate to introduce into the flour a hydrogen peroxide equivalent content of from 0.0005% to a few hundredths of a percent of the flour weight.

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