United States Patent Office

3,085,014

Patented Apr. 9, 1963

3,085,014

METHODS FOR OXIDATIVELY TREATING FLOUR

Herbert O. Renner, 332 N. Wolf Road, Des Plaines, Ill.

No Drawing. Filed June 23, 1959, Ser. No. 15,783
5 Claims. (Cl. 99—91)
(Filed under Rule 47(b) and 35 U.S.C. 118)

This invention relates to the treatment of cereal flours and particularly to an improved process for oxidatively treating flours to accomplish bleaching and/or maturing thereof.

Both maturing and bleaching of flours result 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. Numerous oxidizing agents have been proposed for maturing and bleaching flours. Of these prior 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. The only unobjectionable agent known prior to the present invention and capable of both maturing and bleaching flours is chlorine dioxide. 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.

The present invention employs a single composition capable of both maturing and bleaching flours, and, in certain embodiments, the invention is adapted to accomplish maturing alone. The invention has a number of important advantages in addition to such flexibility of result. One primary advantage is the fact that the invention does not require such precise control of the amount of oxidatively active material as has been necessary with chlorine dioxide. Thus, my invention makes possible the successful treatment of flour without involving excessive danger of damaging the flour by overtreatment. A further major advantage of my invention is its ability to gently treat flours in a manner which may be characterized as "accelerated natural aging." In this connection, bread baked from flour treated in accordance with the invention has an unusually good, natural wheat flavor and excellent natural aroma. Another distinct advantage of the present method is that it employs no materials which are deleterious to human beings. Further, the invention is unique in that it makes possible adequate treatment of the flour with only a very minimum of residual chemical agents being detected in the flour after treatment. In this connection, all embodiments of the invention involve at most the addition of only insignificant proportions of non-food materials capable of surviving baking, and certain embodiments of the invention make it possible to treat the flour in such a manner that there will be no residue whatsoever of treating agent after baking.

The present invention is based upon the use of certain oxidatively active reaction mixtures derived from acetone and hydrogen peroxide. In this specification, I employ the term "oxidatively active" to designate the ability of such compositions to at least mature flour when employed in proportions providing a hydrogen peroxide equivalent on the order of 0.001% of the weight of the flour. Thus, within he meaning of this term, neither hydrogen peroxide nor acetone, taken singly, are oxidatively active. Hydrogen peroxide alone can be added to wheat flour in proportions as high as 2.5% by weight (as 100% H_2O_2) without obtaining any maturing or bleaching effect whatsoever. In fact, it is my experience that hydrogen peroxide alone cannot bleach or mature flour, regardless of the proportions employed, without damaging the baking quality of the flour. Similarly, acetone alone has no desirable effect upon flours. I have discovered, however, that flours are matured and bleached when contacted both by hydrogen peroxide and acetone in accordance with the invention.

This phenomenon can be demonstrated by a simple procedure. A small amount of flour oil, containing the carotinoid pigments of the flour, is placed in an open, shallow dish in a closed desiccator along with a similar dish containing hydrogen peroxide. If this arrangement be left standing for a prolonged period, as long as several weeks, it will be found that some of the hydrogen peroxide has been taken up by the flour oil. This can be determined by titration, or the peroxide can even be washed out of the oil. However, no bleaching of the oil will occur. If the flour oil, containing the hydrogen peroxide, is now exposed to acetone for several hours, the acetone will be taken up by the oil, and the oil will be noticeably bleached. Thus, while the hydrogen peroxide alone does not bleach the oil, bleaching does result when both hydrogen peroxide and acetone are present in activated form.

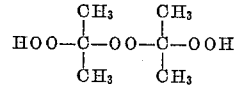
Such a procedure is demonstrative only, the amounts of hydrogen peroxide and acetone actually gotten into the flour oil in this manner being fairly small, so that only a small amount of oxidatively active reaction mixture can result. In actual practice in treating flour, I contact the flour with reaction mixtures of hydrogen peroxide and acetone prepared by aging fresh mixtures of acetone and hydrogen peroxide, with or without the presence of an acid catalyst, under conditions of controlled temperature and time. Using such reaction mixtures, I am able to bring the flour to be treated into immediate proximity with the oxidatively active agents under conditions resulting in effective oxidative treatment of the flour.

The oxidatively active compositions of my invention are prepared by aging mixtures of acetone and hydrogen peroxide for a length of time which varies inversely as the temperature and the amount and activity of the catalyst, if a catalyst be employed. The speed and extent of the reaction is also dependent upon the concentration of hydrogen peroxide, both in the aqueous solution thereof initially employed and in the total reaction mixture. Employing 35% aqueous hydrogen peroxide with approximately molar proportions of acetone and hydrogen peroxide, with no catalyst and using a minimum temperature of about 4° C., the reaction proceeds very slowly and the time period can be as long as many weeks. Using a maximum of about 2% by weight of an acid catalyst and an elevated temperature not above the boiling point of the reaction mixture, usually below 100° C., the reaction period is shortened to as little as a few seconds, depending upon the temperature and the effectiveness of the catalyst. Using molar proportions of acetone and 35% aqueous hydrogen peroxide, the ranges of variables are as follows:

Temperature (° C.)	Catalyst (% by weight)	Time
4	None	2–50 weeks.
4	0.1 (phosphoric acid)	24 hrs.–2 weeks.
Room	None	1–2 weeks.
Do	1.0 (weak acid)	½–12 hours.
Do	1.0 (phosphoric acid)	30–90 minutes.
Do	1.0 (hydrochloric acid)	10–30 minutes.
Boiling point	None	30 min.–several hrs.
Do	0.1 (phosphoric acid)	several minutes.
Do	2.0 (phosphoric acid)	several seconds.

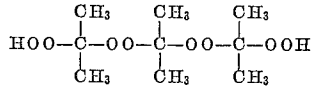
Compositions prepared by aging acetone-hydrogen

peroxide mixtures in the manner just described can be characterized as (1) exhibiting oxidative activity as hereinbefore defined, (2) having a substantial titratable peroxide content afforded by acetone peroxides other than cyclic acetone peroxide polymers, (3) being substantially free from crystallized cyclic acetone peroxide polymers and (4) containing a material proportion of bis-(1,1'-hydroperoxy 1,1'-methyl) diethyl peroxide:



Such compositions also may contain material amounts of unreacted acetone and hydrogen peroxide, which unreacted compounds can be partially or substantially completely removed. When my novel bleaching and/or maturing compositions are hereinafter referred to, it is to be understood that such reference is meant to include the compositions with or without the unreacted starting materials.

Bis-(1,1'-hydroperoxy 1,1'-methyl) diethyl peroxide is, by itself, an effective and valuable agent for bleaching and maturing flour and its incorporation in flour constitutes an important aspect of the present invention. However, compositions prepared as above described contain other acetone peroxides which contribute to the effectiveness of my method, such compounds including the corresponding dihydroperoxy trimer:



and compounds as yet unidentified.

The aging conditions above described have been found to bring about the desired state of oxidative activity while substantially precluding formation of crystallized cyclic acetone peroxide polymers and, of especial importance, without causing side reactions which would consume hydrogen peroxide to produce other compounds, useless for treating flour, such as pyroracemic acid, acetol and acetic acid. The several variables involved can obviously be adjusted to provide a great many combinations of aging conditions. The particular set of conditions employed depends upon the particular use to which the composition is to be put. Thus, in some instances, it is possible to prepare a composition in accordance with the invention and store the same at room temperature with the knowledge that the composition will be used at the end of a given time on the order of from several hours to several days, this "delay period" before use being selected in accordance with the range of aging conditions above referred to. In other cases, the composition may be prepared and converted to active condition by a selected aging procedure, the active composition then being held in cold storage for any desired length of time prior to use. In such cases, storage temperatures on the order of 0–5° C. are effective to minimize further aging, thereby delaying formation and precipitation of cyclic acetone peroxide polymers. In still other cases, it is advantageous to form the reaction mixture under conditions such that the acetone and hydrogen peroxide, with or without catalyst, are continuously fed at selected rates to a mixing zone, the resulting mixture then being fed continuously into a heating zone, and the reaction mixture then charged continuously into the material to be treated. The heat-aged liquid can advantageously be run through a cooler before introduction to the material to be treated. Alternatively, heating may be carried out in the mixing zone. In such cases, the throughput time in the heating zone may be on the order of several seconds, with temperatures of the reaction mixtures on the order of 75–100° C.

When the acetone-hydrogen peroxide mixtures are aged by heat, the volatile acetone should be substantially completely retained in the system, both to prevent loss

of reactive acetone and to limit variations in relative proportions. In order to accomplish such retention, I reflux the volatile components continually to the mixture. In this connection, I have found it to be advantageous to condense the vapors of the volatile components substantially at the surface of the liquid system being aged, so that prompt refluxing occurs at the surface. This prevents any significant losses of the oxidative power of free hydrogen peroxide by vapor phase oxidation of acetone at elevated temperature to useless reaction products. In preparing the aged mixtures, the primary considerations are (1) to obtain sufficient oxidative activity to accomplish the desired effects in the flour to be treated, (2) to obtain stability, that is, maintenance of activity over a prolonged period, and (3) to obtain the composition in such form that it can be intimately and effectively associated with the material to be treated, by procedures which are practical for commercial use. These considerations can be satisfied with the systems in liquid and/or vapor form, or with the systems supported on particulate carriers.

Once the desired organic peroxide activity is obtained, it can be measured by determining the titratable peroxide content. Thereafter, stability of the aged systems is evidenced by the characteristic of maintaining a satisfactory titratable peroxide content over prolonged time periods, when properly stored, so that such systems need not be used promptly after preparation. Both liquid compositions and those supported on particulate carriers have been prepared which were stable over periods on the order of from several weeks to several months.

The relative proportions of acetone and hydrogen peroxide employed in preparing my compositions are selected from the weight-ratio range of from about 100:1 to about 1:20.

A practical procedure in batch operations for determining the required amounts of acetone and hydrogen peroxide for treating a specified amount of flour is to first determine by experimental flour-treating and baking tests with the particular flour to be treated the optimal hydrogen peroxide equivalent (i.e. the quantity by weight percent of flour, of peroxide titrated as hydrogen peroxide) of an aged acetone-peroxide reaction mixture selected on the basis of known performances. After said hydrogen peroxide equivalent has been established, the amount of hydrogen peroxide required for treating a commercial-size batch of flour is calculated and the required corresponding amount of acetone computed on the basis of the acetone-hydrogen peroxide ratio present in the aged reaction mixture selected. If aged acetone hydrogen peroxide reaction mixtures are produced in continuous operation, only the proper setting of a proportioning device is required to deliver the required amounts of acetone and hydrogen peroxide solution, including the necessary aging catalysts, on the basis of the ratio of the two components present in the aged reaction mixture selected and the amount of flour to be continuously treated within the unit of time.

The aging catalysts suitable for use in preparing the oxidatively active compositions of my invention are the edible acid catalysts having a dissociation constant of at least about 6×10^{-10}. Of such catalysts, I find that the strong mineral acids are markedly superior, phosphoric acid and hydrochloric acid being particularly advantageous for many embodiments of the invention.

In this connection, it is to be noted that hydrogen peroxide in aqueous solution seems to dissociate to form hydrogen ions and that commercial grades of both acetone and hydrogen peroxide frequenty contain small proportions of acid. Depending upon the aging conditions selected, such acid content can be effective to satisfactorily promote aging without further catalyst addition.

Typical acid catalysts suitable for the invention, besides hydrochloric, phosphoric, sulfuric and nitric acid, include iodic acid, bromic acid, pyrophosphoric acid, acetic

acid, boric acid, lactic acid, and pyruvic acid. Acid salts, such as sodium acidpyrophosphate, for example, are suitable.

Where iodic or bromic acid is to be used as the aging catalyst, the acid may be produced directly in the liquid system by adding elemental iodine or bromine to the liquid so that the iodine or bromine is oxidized by the hydrogen peroxide. In this connection, it is to be noted that both iodine and bromine are readily soluble in acetone.

The more strongly ionized acids, such as the mineral acids, have a greater catalytic effect in bringing about the desired state of oxidative activity in my compositions than do the weakly ionized acids, such as boric acid. It is accordingly possible to pre-select the aging time and temperature by choice of the acid catalyst and its concentration. Thus, in a process for continuously producing oxidatively active compositions in accordance with the invention, where aging is desirably effected quickly, I may use a relatively large proportion of a relatively strongly ionized acid. On the other hand, if the particular commercial situation involved allows slow againg, I may employ a more weakly ionized acid or, in some instances, no catalyst at all.

The catalysts may be employed in proportions in the range of 0–2% by weight of the reaction mixture.

The acid catalysts have been referred to as edible and, in this connection, it will be understood that only the relatively minute quantities of catalyst employed are considered in dealing with the question of edibility. Thus, all of the strong mineral acids, for example, are edible in small quantity. The acid catalyst employed need not be permanently incorporated in the acetone-hydrogen peroxide system, it being sufficient if the catalyst and the system be maintained in intimate contact during the aging period.

As later discussed in detail, the compositions of my invention can be advantageously supported on various carriers such, for example, as corn starch. In this connection, it should be noted that acid constituents of the carrier are catalytically effective in promoting reactivity of the acetone peroxide mixture. Commercial food grade corn starches, for example, frequently show a pH on the order of 4.8. Both commercial corn starch and commercial wheat starch may contain as much as 0.02% by weight of acid, computed as HCl, such acid content often being the result of the use of sulfurous acid in treatment of the starch during manufacture.

The purpose of the acid catalysts is to effect a more rapid aging of the reaction system, while precluding, or at least greatly minimizing, the tendency to form crystallized acetone peroxide polymers, and the tendency toward side reactions which would consume hydrogen peroxide without producing any product capable of bringing about a desired oxidative change in organic food materials. Thus, a primary attainment of the process of my invention is to age without converting the hydrogen peroxide to ineffective compounds. In this regard, the aging conditions of time, temperature and acid proportion hereinbefore recited are of particular importance.

While, in some procedures for producing the oxidatively active compositions of the invention, it is advantageous to incorporate the acid catalyst in the initial liquid system, other procedures involve addition of all or a part of the catalyst after some againg has been accomplished. Thus, the acetone-hydrogen peroxide mixture can be initially aged by heat alone, or even by storage at room temperature, and a proportion of acid catalyst then added, at the time the composition is to be used, to complete the aging procedure. Similarly, a portion of the catalyst may be added initially, the remainder being added toward the end of the aging period. In such procedures, the first proportion of catalyst may advantageously consist of one acid, and the second proportion of a different one.

I find that, while those edible acid catalysts having a dissociation constant of at least 6×10^{-10} are useful in preparing compositions for use in the invention, certain of such catalysts are individualistic in their effect. Thus, the mineral acids are distinctly more effective. Phosphoric acid and hydrochloric acid are more desirable than sulfuric acid and nitric acid, and phosphoric acid is superior as a catalyst for inclusion in the initial reaction mixture, while hydrochloric acid is superior for subsequent addition.

I have found it to be advantageous to prepare compositions for use in accordance with the invention wherein the reaction product mixture is supported on a solid, particulate, edible carrier. Carrier-supported compositions of this nature are particularly useful for several reasons. A carrier-supported system is often more easily handled and more effectively distributed in some types of food materials than is a liquid system. Perhaps more important, however, is the fact that, when a reactive liquid system of acetone and hydrogen peroxide is uniformly deposited on a particulate carrier, the resulting composition is more stable than the liquid system per se. The carrier-supported systems in general show less tendency toward the production of the cyclic polymeric acetone peroxides, and may be stored for longer periods with less concern as to temperature.

Solid, particulate, edible carriers which are suitable for the invention include food starches, heat-modified food starches, dextrines, wheat flour, defatted wheat flour, heat-treated wheat flour, pre-oxidized starches and flours, wheat gluten, vegetable proteins, such as soybean protein, and edible inorganic materials such as inorganic phosphates and calcium sulfate, which are inert to peroxides. The particular carrier employed should provide a porous structure or a large effective surface area so that the oxidatively active materials can be retained by absorption and/or adsorption.

Carrier-supported compositions can be prepared by first aging the liquid system of acetone and hydrogen peroxide and then uniformly distributing the aged liquid system on the particulate carrier. Alternatively, part or all of the aging can be carried out after the acetone-hydrogen peroxide system has been distributed on the carrier. While most aging procedures within the limits hereinbefore mentioned can be carried out after depositing the liquid system on the carrier, I have found it particularly advantageous to first preliminarily age the liquid system, as by a heat treatment, or by use of both heat and a small proportion of acid catalyst, or by catalytic aging without heating, then add a final quantity of acid catalyst to the preliminarily aged liquid system, and then deposit the preliminarily aged system on the carrier.

Rather than using solid carriers, I may employ liquids as the carrier materials. In particular, I find it advantageous to employ relatively non-volatile organic liquids which are substantially inert to active oxygen. Thus, paraffin oil is an excellent liquid carrier material. In this connection, it is to be understood that the paraffin oil or the like serves only as a carrier for the active acetone-hydrogen peroxide system, with such system being capable of emitting or forming oxidatively active vapors. When such a composition is employed to treat food material, the carrier liquid is not introduced into the food material.

As will be understood by those skilled in the art, it is difficult to prepare acetone-hydrogen peroxide reaction systems in accordance with the invention which do not contain at least a certain amount of water, it being most practical to work with aqueous hydrogen peroxide solutions containing 30–50% peroxide. In some instances, it is advantageous to reduce the water content of the active system and so concentrate the system as to acetone and peroxide. For this reason, I have found it useful to employ a carrier, such as calcium sulfate-semihydrate, for example, which, because of its chemical water-binding capabilities, is able to take up some of the water from the liquid system. Similarly, carriers such as dry

gluten, which are capable of physically binding water, are also advantageous.

The tendency of dry gluten to be hydrated by the water in the liquid acetone-hydrogen peroxide system is also important in another respect. When the carrier contains gluten, agitation of the carrier with the liquid systems causes the formation of small lumps or granules which bind the oxidatively active components so that activity is retained for prolonged periods. The reaction systems can thus be distributed on wheat flour, with the result that hydration of the gluten of the flour causes formation of lumps or granules, and the lumps may be separated out as a concentrated, relatively highly stable, oxidatively active system. Such lumps can be used, for example, in treating unbleached flour and are particularly advantageous because, after bleaching and/or maturing has been effected, the lumps can be sieved out of the treated flour. Alternately, such oxidatively active lumps or granules can be prepared and ground to relatively fine particles before use, such particles then being allowed to remain in the material treated therewith.

Another useful carrier-supported composition can be prepared in accordance with the invention by using small pellets or pre-forms of flour from dried, washed gluten or of high gluten flour, such as that employed in making macaroni. These pre-forms are sprayed with an oxidatively active acetone-hydrogen peroxide reaction system, so that the pre-forms take up and hold the liquid. The amount of liquid employed can be made such that each pre-form is supplied with a quantity of liquid less than the maximum which the pre-form could retain. The partially impregnated pre-forms are then allowed to remain until the liquid has diffused into the interior, and are then introduced into wheat flour or the like to be treated. After the treatment is complete, the pre-forms may be sieved out. In such cases, the pre-forms will have a considerable residual oxidative activity which is not released without the presence of water. They may be ground to fine particle size and used, for example, as an additive for bread dough, wherein their residual activity is released.

Carriers such as starch and flour are of course themselves subject to oxidative changes, so that some of the acetone-peroxide system deposited thereon necessarily is used up initially by the carrier. However, the loss of activity resulting from this is small in view of the relatively large proportion of liquid supported on the carrier and, after initial oxidation of the carrier material, the carrier is effectively inert.

As a modification of the invention involving the use of carriers, I may support the hydrogen peroxide alone upon the carrier material, then blend the carrier with the flour to be treated, and finally pass acetone vapors into the flour while the carrier remains therein. Because of the strong affinity between acetone and hydrogen peroxide, the acetone will be taken up by the hydrogen peroxide upon the carrier, so establishing the desired acetone-hydrogen peroxide system. It should be noted that my invention does not require a full aging of the acetone-hydrogen peroxide reaction system before the system is incorporated in the flour, so long as precaution is taken to avoid the hydrogen peroxide being absorbed as such by the flour. As has been pointed out, flour takes up large amounts of hydrogen peroxide very readily without beneficial effect upon the flour. But, with the hydrogen peroxide supported on a carrier, this tendency is minimized, the hydrogen peroxide being retained by the carrier preparatory to introduction of the acetone vapors. Then, when the acetone vapors have been introduced, the acetone-hydrogen peroxide system is established and will become oxidatively active even though the flour is present.

Also, I may prepare a liquid acetone-hydrogen peroxide system which has been aged as hereinbefore explained, and inject such liquid system directly into the flour to be treated, while agitating the flour to assure uniform distribution. In such case, I find it desirable to employ a "chain blending" procedure, that is, to inject the liquid into only a portion of the flour, say 50% thereof, and then uniformly combine this portion with the remainder of the flour to be treated. Since aging of the liquid system can be accomplished quite rapidly, this embodiment of my invention can be carried out continuously. Thus, the flour to be treated is passed through an agitating zone, the acetone and hydrogen peroxide, with or without a small proportion of acid catalyst, are continually mixed by suitable proportioning devices and the liquid mixture passed through a heating zone maintained at a temperature such that the liquid mixture is heated to a temperature usually not exceeding about 100° C., and the liquid system so prepared is, preferably after proper cooling, continuously injected into the flour in the agitating zone.

Using carrier-supported acetone-hydrogen peroxide reaction systems, my method simply involves the preparation of a carrier-supported composition of the desired concentration as to hydrogen peroxide equivalent, and the uniform blending of this composition with the flour to be treated. Where a carrier of fine particle size is employed, such as starch, wheat flour, etc., the carrier-supported composition is left in the flour. Where the carrier is in the form of relatively larger bodies, such as absorbent pellets and like pre-forms, the carrier-supported composition is removed from the treated flour, as by sieving, before the flour is used.

Ordinarily, whether the oxidatively active composition is used as a liquid sprayed directly into the flour, or in the form of a carrier-supported composition blended with the flour, the amount of the composition is selected to provide a hydrogen peroxide equivalent value on the order of a few thousandths of a percent of the weight of the flour. In fact, for maturing some flours, the amount can be less than 0.001%. When full bleaching is required, the amount of hydrogen peroxide equivalent provided by my compositions may be on the order of 0.006% or even considerably higher. In this connection, it must be noted that the requirements for oxidatively treating flours vary with the particular type of flour. Thus, when dealing with "high extraction flours," containing more of the total wheat kernel, the proportion of hydrogen peroxide equivalent necessary for satisfactory bleaching might be 0.006% of the flour weight. But, with "low extraction flours," a value as low as 0.002% might give a satisfactory bleach, and satisfactory maturing might be accomplished with a hydrogen peroxide equivalent content on the order of 0.0005% of the weight of the flour. As a general range, therefore, the proportion of hydrogen peroxide equivalent provided can vary from a fraction of a thousandth of a percent to several hundredths of a percent of the flour weight, depending upon the type of flour being treated and upon whether only maturing, or both bleaching and maturing, is desired.

The following example illustrates a suitable procedure for preparing and analyzing oxidatively active compositions useful in accordance with the invention:

Example 1

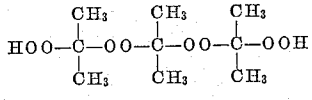
Twenty-five parts by volume of aqueous hydrogen peroxide solution (30% H_2O_2) is blended with 50 parts acetone and 0.05 part concentrated sulfuric acid and the mixture aged for 1 hour at room temperature. At the end of that period, the reaction mixture is a clear liquid free from solids.

Preparatory to demonstrating bleaching and maturing ability of the resulting reaction mixture, a carrier-supported composition is prepared by blending 20 ml. of the liquid reaction mixture with 50 g. food grade corn starch. The resulting carrier-supported composition is blended with unbleached bread wheat flour, using an amount of the carrier-supported composition providing, in the treated

flour, a titratable hydrogen peroxide equivalent content of 0.006% by weight of the flour. Assuming the unbleached flour to have a carotene content of 2.8 p.p.m., the treated flour will be found to have a carotene content of 1.0–1.15 p.p.m. at the end of 10 days, indicating a substantial bleach. If the flour so bleached is now used to bake white bread in the usual manner, employing the same untreated flour to bake control loaves for comparison, it will be found that the loaves baked from the treated flour have greater volume and better texture than the control loaves, and that the dough prepared from the treated flour is more lively and elastic than that prepared from the untreated flour, demonstrating that the carrier-supported oxidatively active composition effectively matured the flour.

A second portion of the liquid reaction mixture is subjected to analysis as follows: The entire portion is extracted with pentane in four steps, each extraction step employing a volume of the solvent equal to twice the initial volume of the reaction mixture sample, the four extracts being combined and kept at room temperature. The extract is then back-extracted with an equal amount of water, resulting in precipitation of a negligible amount of cyclic triacetone peroxide, which is discarded. Pentane extraction of the resulting aqueous solution is repeated in the manner just described, the extract being recovered and the aqueous residue discarded. The pentane extract is then fractionated by conventional column chromatography, using a diatomaceous earth column and eluting in three stages, stage A employing pentane as the eluent, stage B employing a mixture of 5% pentane and 95% acetone and stage C employing a mixture of 10% acetone and 90% pentane. The solution obtained from stage B contains no organic peroxides and that from stage C contains only a negligible proportion of organic peroxides, primarily cyclic triacetone peroxide. The solution obtained by eluting stage A contains 80–85% of the total peroxide content of the pentane extract.

The solution obtained in stage A is subjected to fractional crystallization, the first fraction, representing 70% of the total peroxide present in the stage A solution, being a white, crystalline material melting at 36° C. Analysis of this material by infrared spectrophotometry, polarography, and titration for internal and external peroxide content, indicates that the product is bis-(1,1'-hydroperoxy 1,1'-methyl) diethyl peroxide. That compound is synthesized from the corresponding unsaturated ether and a mixed melting point determination carried out. The mixed melting point is 36° C., yielding proof that the first fraction obtained by the fractional crystallization is in fact bis-(1,1'-hydroperoxy 1,1'-methyl) diethyl peroxide. Carrying the fractional crystallization further, only one additional compound is recovered in pure state, this compound, present in amounts equal only to a very minor proportion of the total peroxide of the stage A solution, converts promptly to cyclic triacetone peroxide and exhibits the characteristics of the linear trimeric dihydroperoxy acetone peroxide:



By such analytical procedure, it can be shown that the acetone-hydrogen peroxide reaction mixtures produced by aging under the conditions hereinbefore defined always contain a material proportion of bis-(1,1'-hydroperoxy 1,1'-methyl) diethyl peroxide, such proportion varying from a few percent to a maximum of about 25% by weight of the total titratable peroxide content of the reaction mixture, depending upon the degree of aging. The amount of bis-(1,1'-hydroperoxy 1,1'-methyl) diethyl peroxide present in the reaction mixture increases as the aging time, temperature and catalyst proportions and strength are increased.

Of the remaining titratable peroxide content of the reaction mixture, a substantial proportion, usually about 10%, is hydrogen peroxide. The major proportion, however, consists of acetone peroxides, primarily hydroperoxidic, as yet unidentified. The unidentified peroxides amount to as much as 65% by weight of the total titratable peroxide content of the reaction mixture and have been found to contribute strongly to the flour bleaching and maturing capabilities of the reaction mixtures.

The following examples are illustrative of various embodiments of the invention:

Example 2

(*a*) An initially unreactive liquid system was prepared by blending 60 cc. aectone with 30 cc. aqueous hydrogen peroxide (33.27%), so that the system consisted by weight of 14.19% hydrogen peroxide, 58.42% acetone and 27.39% water. This liquid system was then heat-aged by passing the same continuously, at a rate of 0.25 cc. per second, through a tube maintained at 113–116° C., the output being continuously condensed and cooled. The aged reaction mixture was then stored for 109 days at about 4–5° C. Titrated activity, as hydrogen peroxide, was found to be exactly the same at the end of the 109-day storage period as at the start thereof.

The liquid reaction mixture was then diluted with acetone at a rate of 1:19 by volume to give a liquid system containing by weight 0.80% hydrogen peroxide, 97.6% acetone and 1.5% water. Thus, the acetone-to-hydrogen peroxide weight ratio of the final oxidatively active composition was 122:1.

(*b*) Twenty-four cc. of this diluted oxidatively active liquid system was sprayed under pressure through a nozzle into 3000 grams of unbleached bread flour while the flour was being agitated in an enclosed mixer. This amount of composition had a hydrogen peroxide equivalent content amounting to 0.006% of the weight of flour being treated. Potassium iodide test was negative after 17 hours storage. Determination of the extent of bleach (by the Pekar or "slick" test) showed only a moderate degree of bleaching. However, when the treated flour was baked into bread, and the bread compared with bread baked from untreated flour, a very good maturing effect was observable.

This example illustrated that the acetone-hydrogen peroxide reaction mixtures of my invention display advantageous maturing power, and a limited bleaching effect, when the acetone-hydrogen peroxide ratio is as high as 122:1 and the liquid composition is directly introduced into the flour to be treated.

Example 3

A particularly advantageous carrier-supported composition for treating flour was prepared as follows: an initial acetone-hydrogen peroxide mixture was prepared by blending 175.0 cc. aqueous hydrogen peroxide (39.3%) with 262.5 cc. acetone and 1.05 cc. 5% phosphoric acid solution to give a liquid system containing by weight 16.59% hydrogen peroxide, 52.29% acetone, 31.11% water and 0.0125% H_3PO_4. During mixing, the liquid system warmed from room temperature to 40.3° C. and was then stored for 24 hours. Aging was then completed by adding 0.0125% by weight HCl. The resulting aged, reactive system titrated 16.46 grams hydrogen peroxide equivalent per 100 cc.

A carrier supported composition was then prepared by mechanically working 396 cc. of this reactive liquid system with 1200 grams of powdered, food grade corn starch. Volatile matter was allowed to escape freely during the mechanical working period of 5 minutes, and the volatiles lost amounted to approximately 20% of the total acetone employed. After a 5 minute working period, the composition titrated 44.16 grams hydrogen peroxide equivalent per 1000 grams.

The carrier-supported composition so prepared was

found to be of sufficient stability to allow its use in various commercial operations. The following tabulation illustrates the prolonged storage periods possible with the composition:

Days Storage	Grams H_2O_2/1,000 Grams	
	Storage at 4° C.	Storage at Room Temp.
1	----------	45.0
7	43.9	43.8
17	44.3	39.9
42	43.8	6.4
66	43.3	0.17
135	43.3	----------
254	41.4	----------

It is thus obvious that the composition can be stored for extremely long periods under conventional refrigeration with insignificant losses of peroxide activity. Similarly, the composition can be stored at room temperature for periods on the order of two weeks and longer.

To demonstrate effectiveness of the composition, 2 grams of the concentrate which had been kept for 135 days at 4° C. was blended with 3000 grams unbleached bread wheat flour. The 2 grams of oxidatively active system provided a hydrogen peroxide equivalent amounting to 0.003% of the weight of the flour. To determine the effect of prolonged contact between the flour and the oxidatively active composition, the treated flour was stored for 132 days at room temperature, and test bakes were then made, preparing the dough by the sponge-dough method. The resulting bread showed excellent bleach, a very fine, uniform grain, a very desirable silky texture, excellent ovenspring, smooth break and good odor.

This example has been included to indicate a number of characteristic features of the invention. First, it will be noted that, in preparing the oxidatively active reaction mixture, a relatively short aging period was employed, this having been made possible by the inclusion initially of 0.0125% of phosphoric acid, and by a later addition of 0.0125% of hydrochloric acid. Even these very small amounts of acid catalyst serve to bring about the desired oxidative activity quickly, so that heating need not be employed. Further, the composition of this example showed no tendency to form solid acetoneperoxide polymers at any time during the procedure. The second stage catalyst addition serves not only to hasten aging, but also to increase the rate at which the oxidative activity is released in contact with the organic material being treated. The example illustrates the important factor of relatively high stability of the compositions under commercially feasible conditions, and the fact that flour treated with the compositions can be stored for prolonged periods without adverse results.

Example 4

An initial liquid mixture was prepared by blending 24.8 cc. of the heat-aged and acetone-diluted liquid composition of Example 2(*a*) with 1.24 cc. of a freshly prepared mixture of 14.19% hydrogen peroxide, 58.42% acetone and 27.39% water having been only heat-aged by the procedure of Example 2(*a*).

Three thousand grams of unbleached bread wheat flour was treated with 24.4 cc. of this oxidatively active composition as follows: The full 24.4 cc. of active liquid composition was first incorporated in 1700 grams of the flour in a mechanical paddle type blender, the mixture being thoroughly agitated for 10 minutes. This amount of treated flour was then immediately combined with the remaining 1300 grams of flour and the mixture uniformly blended. By this procedure, the 24.4 cc. of oxidatively active composition provided a hydrogen peroxide equivalent of 0.012% of the weight of the flour, with assurance of uniform distribution.

After 3 days storage, the treated flour gave a negative test for free peroxide and showed a pronounced bleach. After 6 days storage, the treated flour was used to prepare bread by the straight-dough method, the bread showing satisfactory crumb color with loaf volumes and ovenspring indicating pronounced flour-and-dough maturing.

It is thus apparent that compositions in accordance with the invention are effective even when only a relatively low proportion of hydrogen peroxide is employed in preparing the reactive acetone-hydrogen peroxide system. In this connection, it is to be noted that the primary consideration is that enough of the reactive system be employed, in treating the organic food material, to provide a titratable peroxide content of the desired proportion relative to the quantity of flour being treated.

Example 5

To demonstrate the preparation of active compositions relatively rich in peroxide, 75 cc. of aqueous hydrogen peroxide solution (39.2%) was mixed with 25 cc. acetone, and this mixture then heat-aged by a batch procedure in which the mixture was heated to 74.5° C. in 20 minutes, held at that temperature for 70 minutes and then rapidly cooled to room temperature. The aged liquid system was then diluted with acetone to bring the acetone-to-hydrogen weight ratio to 1.36:1. To indicate stability, the aged and diluted liquid composition was kept at room temperature until the first sign of crystalline polymeric acetone peroxide formation, requiring a period of 113 hours.

A carrier-supported composition was prepared by working 100 cc. of the 20-hour old liquid reaction mixture into 200 grams of dry, powdered, food grade corn starch, thus forming a crumbly mass having a sharp, active horseradish-like odor indicative of the presence of bis-(1,1'-hydroperoxy 1,1'-methyl) diethyl peroxide. After four days at room temperature, this composition titrated 89.7 grams hydrogen peroxide equivalent per 1000 grams and, after 25 days at room temperature, 79.6 grams per 1000.

Unbleached wheat flour was treated with the 25-day old starch-supported composition as follows: Using a mortar and pestle, the starch-supported composition was worked into 1% of the total flour to provide a smooth, dry blend. This material was then uniformly distributed in the remainder of the flour by agitating in a paddle mixer. The amounts of starch-supported composition and flour were chosen to give 0.038 gram of the starch-supported composition for each 100 grams of flour, so that the proportion of hydrogen peroxide equivalent added was 0.003% of the weight of the flour. After 6 days storage, the treated flour gave a negative test for available peroxide and the Pekar or "slick" test showed a very pronounced and satisfactory bleach. Baking tests, using a straight-dough procedure after the treated flour had been stored for 16 days, gave highly elastic, lively doughs and resulted in loaves with excellent crumb color, very soft texture, improved ovenspring and good crust color. A 2% increase in water absorption was noted.

This example illustrated that a high proportion of hydrogen peroxide can be employed in preparation of my oxidatively active reaction mixtures, with the result that a smaller total quantity of the active system is sufficient for treatment of the organic food material. The example also illustrates the relatively great stability of carrier-supported active compositions, since the composition used in treating flour in this example had been stored at room temperature for 25 days.

Example 6

The following procedure additionally illustrates the utility of corn starch as a carrier for my oxidatively active reaction mixtures, and advantageous use of hydrochloric acid as a catalyst. An initial liquid mixture was prepared by blending 30 cc. of 38.27% aqueous hydrogen peroxide

solution, 60 cc. of acetone and 0.68 cc. of 6.6% hydrochloric acid solution to provide a system including by weight 13.99% hydrogen peroxide, 57.92% acetone, 28.03% water and 0.055% HCl. This mixture titrated 12.46 grams hydrogen peroxide equivalent per 100 cc. To prevent any influence of the heat, generated by the mixing step, on aging of the reaction system, the liquid mixture was cooled for 45 minutes before distribution on the carrier.

The carrier-supported system was prepared by adding 24.3 cc. of the liquid mixture in a coarse stream to 1000 grams of powdered food grade corn starch while the starch was being agitated in an enclosed paddle mixer. At the end of three hours' storage in a closed container at room temperature, the resulting composition titrated 2.95 grams hydrogen peroxide equivalent per 1000 grams.

Thirty grams of this composition (providing a hydrogen peroxide equivalent content amounting to 0.0029% of the weight of the flour) was then incorporated in 3000 grams unbleached wheat flour. After storage for one day, the treated flour gave a negative potassium iodide test for available peroxide and showed a very good bleach. After seven days storage, the treated flour was used in baking tests. As compared to control brakes with untreated flour, the tests showed that the flour treatment resulted in additional water absorption of 3% in the dough, with very lively springy, elastic doughs resulting, the baked bread having excellent color, grain, texture and ovenspring, and showing a volume increase of 2.1%. Similar test bakes with the treated flour after 12 days storage resulted in similar results with a volume increase of 5.8%.

Example 7

To illustrate the use of wheat starch as a carrier in accordance with the invention, the following procedure was carried out: 50 cc. of cold hydrogen peroxide (39.4% aqueous solution) was blended with 50 cc. of acetone and the resulting liquid aged at room temperature for 6⅔ days in a closed safety bottle. At the end of this time, 0.51 cc. of 5% phosphoric acid solution, introducing 0.026% by weight phosphoric acid, was added. 10.5 cc. of this aged and acidified liquid composition was then uniformly worked into 125 grams of unmodified, powdered, wheat starch. The wheat starch contained unidentified acidity amounting to 0.0054% as HCl.

After one hour's storage, the resulting wheat starch-supported system showed, by titration, activity equivalent to 15.57 grams hydrogen peroxide per 1000 grams. After 24 days storage this value was 12.40 grams.

Three-thousand grams of unbleached bread wheat flour was treated with 5.8 grams of the 2½ hour old wheat starch-supported acetone-hydrogen peroxide system, providing a hydrogen peroxide equivalent of 0.003%. This was accomplished by first uniformly combining the total amount of the oxidatively active composition with a small fraction of the flour and then uniformly blending the resulting product with the remainder of the flour. After 4 days storage at room temperature, the flour showed a negative potassium iodide test and a Pekar or "slick" test showed the flour to have a pronounced bleach. After 10 days storage, the treated flour was used to bake bread. The resulting doughs were of excellent quality in every respect and the baked loaves showed a very satisfactory bleach, very soft texture and a very good ovenspring.

Example 8

A liquid composition of 29 cc. aqueous hydrogen peroxide solution (24.8% peroxide), 1 cc. of acetone and 0.019 gram of hydrochloric acid (100%) was worked into 50 grams of white dextrine from potatoes, using a mortar and pestle. The resulting composition was a very stiff paste. This was converted to a stiff, fondant-like mass by exposure to acetone vapors in a closed space for 2 hours. The resulting product was dried in open air for 7 days, ground to pass a 40-mesh screen, washed with ethyl ether and dried in vacuo. The dried product was strongly positive to potassium iodide.

This product was diluted with 99 parts by weight corn starch and the resulting composition was incorporated into unbleached bread wheat flour in an amount equal to 0.05% of the weight of the flour. Test bakes showed increased water absorption, doughs which were more springy and elastic and loaves having a silkier texture and a finer grain. Thus, the composition of this example gave excellent maturing effects, but no bleaching was apparent.

Example 9

A liquid composition was prepared by blending the following ingredients in the order given:

	Cc.
Hydrogen peroxide solution (38.3% H_2O_2)	214.0
Hydrochloric acid (6.6% solution)	3.55
Acetone	304.3

This liquid was then aged in a closed container at room temperature for 70 minutes. Four hundred and ninety five cc. of the aged liquid was then incorporated into a total of 11.475 kg. of unbleached Texas wheat flour, using a motorized paddle blender. After 5 hours storage, the resulting composition was reduced to a dry, uniformly particulate product by hammermilling without vapor recovery. This composition showed, by titration, 5.12 grams peroxide activity per thousand grams, as H_2O_2. After 16¼ hours, this value was 4.93 grams, and, after 40 hours, 4.66 grams.

Two thousand two hundred pounds of unbleached Texas bread wheat flour was treated, in a commercial spiral blender, with a quantity of the above flour-supported acetone-hydrogen peroxide composition amounting to 1% by weight of the flour being treated. At this time, the acetone-hydrogen peroxide reaction mixture was 17 hours old and the amount used provided a titratable hydrogen peroxide equivalent value 0.005% of the weight of the flour being treated.

After two days' storage at room temperature, the treated flour was used in bakes, carried out by the sponge dough procedure without bromate. These bakes showed a 1% increase in water absorption, very satisfactory baking characteristics, and a .5% loaf volume increase, as compared to control. Similar bakes carried out after the treated flour had been stored for 9 days showed excellent bleaching, improved grain and texture and a 5.6% loaf volume increase. Samples of the treated flour stored for 188 days still showed a noticeably positive potassium reaction, indicating the presence of stable acetone-hydrogen peroxide factors which did not react with the dry flour but which were apparently effective during baking.

Example 10

A fresh blend of 50 cc. aqueous hydrogen peroxide (39.1% H_2O_2) and 50 cc. acetone was heat-aged in a refluxing heater at 67–70° C. for five hours, then cooled and stored for 18 hours. Unbleached wheat flour was defatted by refluxing for six hours with acetone. Sixty-six cc. of the heat-aged, liquid acetone-hydrogen peroxide reaction mixture, titrating 20.48 grams hydrogen peroxide per 100 cc., was distributed on 1500 grams of the defatted flour, the resulting composition stored for 24 hours, then evacuated for 30 minutes and hammermilled.

Four hours after milling, 13.5 grams of this composition, titrating 6.65 grams hydrogen peroxide per 1000 grams and introducing 0.003% hydrogen peroxide equivalent to the flour, was blended with 3000 grams unbleached wheat flour. After ten days, the treated flour gave a practically negative potassium iodide test and was completely bleached. Straight-dough bakes, made in the absence of bromate with the flour after 34 days storage showed satisfactory doughs, well-bleached crumb, slight loaf volume increase, the other desirable load characteristics.

Similar tests with the acetone-hydrogen peroxide reac-

tion mixture 40 days after its preparation, using 16.3 grams thereof per 3000 grams unbleached flour to again provide a hydrogen peroxide equivalent of 0.003% of the flour weight, gave a complete bleach after four days. Straight-dough bakes after 14 days storage of the treated flour required 2% additional water absorption in the dough, to produce doughs of excellent quality and mellow feel. The baked loaves showed very good bleach, close grain, very soft texture and good ovenspring.

This example is chosen to illustrate the suitability of defatted wheat flour as a carrier, the fact that rather severe heat-aging procedures can be employed, and the feasibility of evacuation and hammermilling without undue loss of flour bleaching activity.

Example 11

An acetone-hydrogen peroxide blend comprising 18.73% by weight hydrogen peroxide, 40.17% acetone, 40.84% water, and 0.26% phosphoric acid (100%), was aged in a closed container at room temperature for 22 hours. Seventeen cc. of the liquid reaction product was worked into 34 grams of wheat flour previously heated in a closed chamber for 23 hours at 80° C. and cooled. Forty-four and seven-tenths grams of the blend was worked into an additional 255.3 grams of the heated flour and the resulting mass flaked between rolls and hammermilled. Of the resulting particulate composition, 12.0 grams (titrating 7.49 grams hydrogen peroxide equivalent per 1000 grams) was blended with 3000 grams unbleached flour. After five days storage, the flour treated with 0.003% hydrogen peroxide equivalent was well bleached. Bakes with the treated flour after 23 days' storage showed excellent, very lively, elastic doughs, and produced loaves with a 4.1% volume increase and excellent loaf characteristics.

Example 12

An initial liquid mixture comprising 12.50% by weight hydrogen peroxide, 57.27% acetone, 30.18% water and 0.05% HCl was stored under refrigeration for 13 days. At the end of this time, 2 cc. of the cold-aged liquid system, titrating 0.262 gram hydrogen peroxide equivalent, was worked into 17 grams of pure wheat gluten, using a mortar and pestle. The resulting product was a dry, flaky but slightly gummy mass comprising 16.2% lumps remaining on a 120 mesh screen, the balance being fines capable of passing a 120-mesh screen. The lumps were separated out and dried in the open at room temperature for 22 hours, at the end of which period the dried product titrated 40.2 grams hydrogen peroxide equivalent per 1000 grams. The dried lumps were then used to treat unbleached wheat flour at the rate of 3.18 grams of the lumps per 3000 grams of flour. This proportion provided in the flour a hydrogen peroxide equivalent amounting to 0.0042% of the weight of the flour. At the end of three days storage, the flour was negative to potassium iodide except for some coarser reactive specks, and was completely bleached. After 13 days' storage, the gluten lumps were removed from the flour by sifting. They still carried activity equivalent to 0.0022% hydrogen peroxide, by weight of flour treated, indicating that complete bleaching was obtained by the 0.002% hydrogen-peroxide equivalent of those factors of the concentrate reactive with the dry flour.

Example 13

An initial liquid mixture was prepared by blending 20.0 cc. of aqueous hydrogen peroxide solution (36.75% H_2O_2) with 40 cc. of acetone. After being aged at room temperature for two days, 10 cc. of the resulting liquid reaction mixture was mixed with 20 grams of secondary calcium phosphate ($CaHPO_4.2H_2O$) to form a semi-dry mass. One hundred grams of unbleached wheat flour was then added as a diluent.

Unbleached wheat flour was then treated with this composition by blending 2.92 grams of the composition (titrating 10.25 grams hydrogen peroxide equivalent per 1000) with 1000 grams of the flour. After three days' storage, the flour reacted positive to potassium iodide and was completely bleached. After 20 days' storage, the flour showed only a negligible reaction to potassium iodide. At the end of this period, straight-dough bakes, without bromates, showed very desirable dough and loaf characteristics, including satisfactory color removal. The secondary calcium phosphate used as carrier is characterized by releasing its activity in contact with flour used as diluent until the activities of both, mineral carrier and flour diluent, are equal.

Example 14

An initial liquid mixture was prepared by blending 30 cc. of aqueous hydrogen peroxide solution (36.75% H_2O_2) with 60 cc. of acetone and 0.68 cc. of 6.6% aqueous hydrochloric acid solution. This acidified mixture was aged in a closed container at room temperature for 25 hours. At the end of this time, 20.4 cc. of the reaction mixture was worked into 23.1 grams of calcium sulfate semihydrate. The resulting soft, putty-like mass was stored in a closed container at room temperature for 2⅔ days to permit setting and to allow the calcium sulfate semihydrate to take up as much water from the liquid system as possible. The resulting product was a hard mass, easily crushed, having a titratable peroxide content equivalent to 37.8 grams hydrogen peroxide per 1000 grams.

Three thousand grams of unbleached wheat flour was treated with 2.54 grams of this composition by first grinding all of the calcium sulfate-supported acetone-hydrogen peroxide composition with 5% of the total flour until the resulting blend passed through an 80-mesh screen and then blending this mixture with the remaining 95% of the flour. After ten days' storage, the treated flour was well bleached and was completely negative to potassium iodide. At this time, the flour was used in straight-dough bakes, without bromate, producing very lively, elastic, mellow doughs and excellent loaves with well-bleached crumb, very desirable grain, soft texture, improved ovenspring and normal wheaty odor similar to that of bread baked from unbleached wheat flour.

It is to be noted that the 23.1 grams of calcium sulfate semihydrate employed in preparation of the composition is theoretically capable of chemically binding 4.38 grams of water.

Example 15

One thousand grams of sucrose and 75 cc. of aqueous hydrogen peroxide solution (30% H_2O_2) were worked into a porous, semi-dry mass which was then exposed, in a closed chamber at room temperature, to vapors from 39.5 cc. of acetone. At the end of three days, the acetone had been entirely absorbed by the sucrose-hydrogen peroxide composition, providing a sucrose-supported system theoretically comprising 18.75% by weight hydrogen peroxide, 25.94% acetone and 55.31% water. This composition was dried in open air at room temperature for one day to form hard lumps having a titratable peroxide content equal to 1.9 grams per 1000 grams. Fifteen grams of the resulting dried composition was then worked, by rubbing, into a small fraction of 1500 grams of unbleached wheat flour and the resulting mixture then blended with the balance of the flour. After 37 days' storage, the flour was well bleached. At the end of this time, straight-dough bakes, without bromate, requiring an additional 6.5% water absorption in the dough, produced lively, elastic doughs and well bleached loaves with very satisfactory grain, texture and ovenspring.

Example 16

An initial liquid mixture was prepared by blending 41 cc. of aqueous hydrogen peroxide (39.1% H_2O_2) and 59 cc. of acetone. This mixture was aged in a closed con-

tainer at room temperature for 42 hours and then acidified with 0.0125 gram hydrochloric acid and 0.0125 gram phosphoric acid. The acidified liquid was then allowed to stand in a closed container at room temperature for 95 minutes. At the end of this time, 63.7 cc. of the time and acid-aged mixture was injected into 1200 grams of unbleached wheat flour (a bakers' patent flour), as a carrier, in a paddle mixer. The resulting carrier-supported system was hammermilled, and, after two hours, titrated 6.73 grams hydrogen peroxide equivalent per 1000. Fourteen and one tenth grams of this composition was blended with 1900 grams of the same poor grade, unbleached wheat flour. The total amount of reaction mixture employed provided a hydrogen peroxide equivalent equal to 0.005% of the flour weight. After 17½ hours' storage, the flour was markedly positive to potassium iodide and showed an excellent bleach. After 19 days' storage, the treated flour was used in straight-dough bakes, requiring an additional 2% water absorption in the doughs and giving excellent doughs which had a dry feel and were springy and elastic. The loaves showed a well-bleached crumb, a 3.3% volume increase and improved grain and texture.

I claim:

1. The method for oxidatively treating flour to at least mature the same comprising incorporating in the flour an effective amount of an oxidatively active acetone-hydrogen peroxide reaction mixture, said reaction mixture being substantially free from crystallized cyclic acetone peroxide polymers and comprising a material proportion of bis-(1,1'-hydroperoxy 1,1'-methyl) diethyl peroxide, said amount of said mixture providing a hydrogen peroxide equivalent content equal to from 0.0005% to a few hundredths of a percent of the weight of the flour.

2. The method for oxidatively treating flour to at least mature the same comprising incorporating in the flour an effective amount of bis-(1,1'-hydroperoxy 1,1'-methyl) diethyl peroxide, said amount providing a hydrogen peroxide equivalent content equal to from 0.0005% to a few hundredths of a percent of the weight of the flour.

3. The method for oxidatively treating flour to at least mature the same comprising introducing into the flour an oxidatively reactive liquid reaction product mixture of acetone and hydrogen peroxide, said reaction product mixture being substantially free from crystallized cyclic acetone peroxide polymers and having a substantial titratable peroxide content other than hydrogen peroxide, which content at least predominantly comprises acyclic acetone peroxides and contains a substantial proportion of bis-(1,1'-hydroperoxy 1,1'-methyl) diethyl peroxide, and agitating the flour to uniformly distribute said reaction product mixture therethrough, said titratable peroxide content amounting to from 0.0005% to a few hundredths of a percent of the weight of the flour.

4. The method for oxidatively treating flour to at least mature the same, comprising introducing into the flour an oxidatively active composition comprising an edible, solid, finely particulate carrier material the particles of which carry a liquid reaction product mixture derived from acetone and hydrogen peroxide, said liquid reaction product mixture being substantially free from solid cyclic acetone peroxide polymers and having a substantial titratable peroxide content other than free hydrogen peroxide, which content at least predominantly comprises acyclic acetone peroxides and contains a material proportion of bis-(1,1'-hydroperoxy 1,1'-methyl) diethyl peroxide, the amount of said composition employed being such as to introduce into the flour being treated a hydrogen peroxide equivalent content equal to 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 introducing into the flour an oxidatively active composition prepared by distributing on an edible, solid, finely particulate carrier material a liquid medium containing acyclic acetone peroxides and substantially free from solid cyclic acetone peroxides, said acyclic acetone peroxides providing in said liquid medium a substantial titratable peroxide content which contains a material proportion of bis-(1,1'-hydroperoxy 1,1'-methyl) diethyl peroxide, the quantity of said composition employed being such that said titratable peroxide content supplies to the flour being treated a hydrogen peroxide equivalent content equal to from 0.0005% to a few hundredths of a percent of the weight of the flour.

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