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PREPARATION OF FLOUR BLEACHING COMPOSITIONS

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This invention relates to flour bleaching compositions which contain solid organic peroxides and to their preparation.

Organic peroxides have long been used as bleaching agents for flour, particularly the solid organic peroxides because they can be finely divided and then readily and intimately admixed with the flour. However, these organic peroxides are quite flammable and easily decomposable even at moderate temperatures, and are explosive under certain conditions. In order to prevent flammability as well as to overcome decomposition during grinding, the solid peroxides have been mixed before grinding with certain inorganic compounds containing substantial amounts of bound water, such as alkali metal aluminum sulfates. On the other hand, these hydrated compounds create a tendency toward dampness which interferes with fine grinding and causes packing or lumping of the ground product. To eliminate these disadvantages, suitable inert anhydrous materials such as dicalcium phosphate, calcium sulfate and the like have been ground with the peroxide and the hydrated compound.

The above mixtures must be finely ground which is an undesirable operation, and further the addition of such compositions to flour results in the introduction of foreign ash. It is known that the ash content of a flour has a considerable effect on the colloidal behavior of the flour proteins affecting the quality or commercial grade of the flour and its doughing and baking characteristics, and hence the introduction even of small amounts of foreign ash is objectionable.

One of the objects of the present invention is to eliminate the grinding required to produce a dry powdery composition by the above procedure.

Another object is to avoid the introduction into the flour of any foreign ash-producing materials such as those used in the above compositions.

A further object is to provide a novel finely divided free-flowing non-flammable bleaching composition containing a solid organic peroxide but introducing no other foreign material into the flour in which it is used.

The above objects are achieved by causing the desired solid organic peroxide to precipitate from solution in the presence of suspended finely divided particles of starchy material such as starch or flour. The desired peroxide may be obtained from any suitable source and dissolved in a suitable solvent, or the peroxide may be formed in situ in the solvent from suitable reactive materials. The peroxide may then be caused to precipitate from its solution in the presence of the

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starchy material in any suitable way. For example, the peroxide solution may be diluted with a miscible liquid in which the peroxide is relatively insoluble until the peroxide comes out of the solution. It is also possible to add reagents to such liquid under conditions which will cause chemical precipitation of the peroxide.

Whatever method of precipitation is employed, the peroxide is obtained in the form of minute particles interspersed with the particles of starchy material, both materials being in suspension. The solid materials are then suitably separated from the liquid and dried preferably to about the normal moisture value of the starchy material in equilibrium with the atmosphere, although it is not necessary to dry to this extent as the starchy material will eventually attain and maintain this moisture level in any event. Practically all of the moisture will be contained in the starchy material because of its imbibing capacity and the hydrophobic nature of the peroxide, and the amount of this moisture will depend on the kind of starchy material used and the atmospheric conditions, varying from about 10% to about 18%. This amount of moisture is sufficient to prevent flammability of the peroxide. The dried product comprises a finely divided powder, usually snow-white in color, with the particles of solid peroxide uniformly distributed and intimately admixed with the starchy particles or starch granules as the case may be.

Any desired starchy material can be used from either tuber or cereal sources. Potato starch has a relatively high moisture value and is well suited for the purpose of the invention, but cereal starches such as wheat starch also give good results. The pure starch from any of these sources provides a product which introduces practically no ash into the flour. However, flour itself may be used as the starchy material to be treated as set forth above and then added back to the flour for bleaching, and although such preparations are not completely ashless, yet no foreign material is introduced into the flour.

Any of the so-called active solid organic peroxides may be used, these including both aromatic and fatty acid peroxides and having sufficient activity in a finely divided state to accomplish the desired bleach. These are all flammable peroxides, but have their flammability entirely prevented by the moisture in the starchy materials. Examples are benzoyl peroxide, furoic peroxide, cinnamoyl peroxide, phenyl acetyl peroxide, lauryl peroxide, stearyl peroxide, etc.

Benzoyl peroxide is preferred, as it is by far the most active of the known peroxides.

The proportion of solid peroxide to starchy material is not critical and may vary widely. In general it is preferred to keep this proportion below about 50% because of the increased hazard at higher proportions. Moreover, since no foreign ash is introduced into the flour, there is no particular advantage in increasing the ratio of peroxide to starch, whereas on the other hand an increase in the proportion of starchy material tends to facilitate admixture of the bleaching composition with the flour. The peroxide is uniformly distributed throughout the starchy material and is efficiently utilized with good results in concentrations of the order of 25–50% but it will be understood that this range is not critical and that the invention is not restricted thereto.

In order to obtain precipitation of the peroxide by dilution of the peroxide solution, any two substances may be used in one of which the peroxide is of limited solubility as compared to its solubility in the other. It will be apparent that such combinations are numerous. For example, methyl alcohol and petroleum ether are useful diluents when the peroxide is dissolved in benzene. Preferably water is used as a diluent, the peroxide being dissolved in a solvent such as acetone, ethyl alcohol, normal or iso propyl alcohol, methyl ethyl ketone, dioxane, etc.

A suitable method of carrying out the process is form an aqueous suspension or slurry of the starchy material, to which a solution of the peroxide in one of the above solvents is then added slowly with stirring, whereby the peroxide is precipitated promptly and is finely dispersed throughout the suspension or slurry. After filtering and drying, the particles of solid peroxide are uniformly distributed throughout the starchy material. This procedure is illustrated by the following examples.

Example 1

Ten grams of benzoyl anhydride were dissolved in 20 cc. of acetone. To this solution first 6 grams of sodium bicarbonate were added and then slowly, with stirring, 6 cc. of 30% hydrogen peroxide. Fifteen minutes were allowed for the reaction yielding benzoyl peroxide. This benzoyl peroxide solution was poured slowly, with stirring, into 150 cc. of water containing 8 grams of wheat starch. The resulting mixture containing both starch and benzoyl peroxide in suspension was filtered, after which the filter cake was washed with copious amounts of water, dried on a watch glass at 30° C., broken into small particles or fragments with a spatula, and sieved through a 25 standard silk. The resulting powder was snow white in color and contained 35% benzoyl peroxide and about 11 to 12% moisture in the starch. One-half gram of this powder was intimately mixed with 1 lb. of unbleached flour yielding a very white bleach in about 24 hours.

Example 2

Ten grams of furoic anhydride were dissolved in 40 cc. of acetone. Six grams of sodium bicarbonate were added to this solution, which was cooled to 0° C., after which 6 cc. of 30% hydrogen peroxide were added slowly, with stirring. Fifteen minutes were allowed for the reaction yielding furoic peroxide. This furoic peroxide solution was poured slowly, with stirring, into 150 cc. of water containing 8 grams of wheat starch. The resulting mixture containing both starch and furoic peroxide in suspension was filtered, after which the filter cake was washed with copious amounts of water, dried on a watch glass at 30° C., broken into small particles or fragments with a spatula, and sieved through a 25 standard silk. The resulting powder was white with a greenish yellow tinge and contained 32% furoic peroxide and about 11 to 12% moisture in the starch. One-half gram of this powder was intimately mixed with 1 lb. of unbleached flour yielding a very white bleach in about 24 hours.

The relative amounts of water and solvent can be adjusted to prevent immediate precipitation of the peroxide, thus allowing time for the peroxide solution to permeate the starch particles so that on subsequent addition of more water the peroxide is precipitated to some extent within the starch particles. The peroxide solution can be preformed and then added to an aqueous starch slurry as in Examples 1 and 2, the amount of water in the slurry being initially insufficient to precipitate the peroxide, or the starchy material can be slurried in the peroxide solution, the mixture being allowed to stand in either case before the addition of more water to precipitate the peroxide. This procedure is illustrated by the following example, but ordinarily the results obtained by immediate precipitation of the peroxide are preferred.

Example 3

Ten grams of waxy (sorghum Cody) starch was slurried in 40 cc. of an acetone solution containing 10 grams of benzoic anhydride and 8 grams of $NaHCO_3$. To this was added, slowly and with vigorous stirring, a solution composed of 8 grams of $NaHCO_3$, 10 cc. of water and 10 cc. of 30% H_2O_2. The whole was then allowed to stand for 15 minutes to insure completion of the reaction and then diluted out by the addition slowly with stirring of 50 cc. of water, whereupon the benzoyl peroxide which was in solution and in contact with the starch was precipitated in situ. The suspension was filtered, washed with copious amounts of water, and sucked dry on the filter plate. Analysis showed a peroxide content of 40% upon allowing the starch-peroxide mixture to dry further in the atmosphere, i. e., allowing the starch to attain its equilibrium moisture content.

In the case of starchy materials containing substantial amounts of proteins, such as flour, it has been found that the solvent for the peroxide has a beneficial influence on the colloidal behavior of the proteins. Thus, where the peroxide solution is added to an aqueous slurry of flour, as was carried out with starch in Examples 1 and 2, the particles of dough originally formed in the flour slurry are effectively prevented from further swelling and cohering and are, in fact, dehydrated so as to overcome their stickiness and minimize their colloidal dispersion. On the other hand, where the flour is slurried in the peroxide solution, as was carried out with starch in Example 3, there is an immediate effect on the proteins which are effectively prevented from hydrating and agglutinating into doughy particles. In either case, the peroxide is properly admixed with the flour and subsequent filtration is facilitated. It is necessary, of course, that the solvent for the peroxide be employed in sufficient amounts to permit it to act on the proteins in the foregoing manner.

Example 4

To 10 grams of cake flour, 10 grams of benzoyl anhydride, and 8 grams of sodium bicarbonate in 40 cc. of acetone was slowly added with stirring 8 grams of sodium bicarbonate in 10 cc. of water and 10 cc. of 30% hydrogen peroxide. After allowing the whole to stand for 15 minutes to insure completion of the reaction, 150 cc. of water was slowly added with continued stirring. After about one hour standing to permit settling, the material was filtered and air dried. The weight of the white, powder-like, air dried material was 14.0 grams. The moisture content was around 11–13%. One gram of the air dried sample when analyzed for peroxide required 28.5 cc. of N/10 sodium thiosulphate. This represents 34.5% benzoyl peroxide.

In the preceding Example 4, some difficulty was experienced due to colloidally dispersed protein. Subsequent tests, however, indicated that this difficulty can be overcome by increasing the ratio of acetone to water either by increasing the proportion of acetone in the original slurry or decreasing the proportion of water for precipitation. Thus, the use of acetone in amounts of the order of 90 cc. or subsequent use of water in amounts of the order of 75 cc. permits easy filtration.

In the foregoing examples, the peroxide was formed in situ by reaction between the anhydride and hydrogen peroxide, the reaction medium being made alkaline by the use of sodium bicarbonate. The latter and also the hydrogen peroxide were used in considerable excess to insure complete use of the anhydride. Other conditions and methods of synthesis may be used in practice, or the peroxide itself may be obtained from usual commercial sources.

In Examples 1 and 2, the bleaching powder was used in much greater quantities than actually required for bleaching. In commercial practice, it is customary to use very small amounts of the bleaching agent for longer periods of time. For instance, 1 lb. of unbleached flour may be mixed with say 0.05 gram or less of the bleaching powder, the desired degree of bleach being reached in 48 hours or longer if necessary.

It will be understood that the invention is not restricted to the above examples and that various changes may be made in the details of procedure and proportions without departing from its spirit. Reference should therefore be had to the appended claims for a definition of the limits of the invention.

What is claimed is:

1. The process of preparing a finely divided bleaching composition for dry admixture with flour to be bleached which comprises forming a solution of benzoyl peroxide, diluting the solution with a precipitant for benzoyl peroxide which is miscible with the peroxide solvent while suspending finely divided starchy material in the liquid mixture to cause precipitation of the peroxide in the presence of the suspended starchy material, and then separating the starchy material and the precipitated peroxide from the liquid suspension and drying the same.

2. The process of preparing a finely divided bleaching composition for dry admixture with flour to be bleached which comprises forming a solution of benzoyl peroxide in a water-miscible solvent, diluting the solution with water while suspending finely divided starchy material in the liquid mixture to cause precipitation of the peroxide in the presence of the suspended starchy material, and then separating the starchy material and the precipitated peroxide from the liquid suspension and drying the same.

3. The process of preparing a finely divided bleaching composition for dry admixture with flour to be bleached which comprises forming a solution of benzoyl peroxide in acetone, diluting the solution with water while suspending finely divided starchy material in the liquid mixture to cause precipitation of the peroxide in the presence of the suspended starchy material, and then separating the starchy material and the precipitated peroxide from the liquid suspension and drying the same.

4. The process of preparing a finely divided bleaching composition for dry admixture with flour to be bleached which comprises forming a solution of benzoyl peroxide in acetone, diluting the solution with an aqueous suspension of finely divided starchy material to cause precipitation of the peroxide in the presence of the suspended starchy material, and then separating the starchy material and the precipitated peroxide from the liquid suspension and drying the same.

5. The process of preparing a finely divided bleaching composition for dry admixture with flour to be bleached which comprises forming a solution of benzoyl peroxide in acetone, suspending finely divided starchy material therein, diluting the solution-suspension with water to cause precipitation of the peroxide in the presence of the suspended starchy material, and then separating the starchy material and the precipitated peroxide from the liquid suspension and drying the same.

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