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BLEACHING OF FLOUR

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The present invention relates to the bleaching of flour, by means of liquid organic peroxides.

It has already been proposed to bleach flour by mixing with it organic peroxides followed by a physical or mechanical treatment, for example, by the action of actinic rays, by warming or stirring, or both. The only practical method of proceeding was to add the organic peroxide to the flour in a more or less finely divided solid condition, although it has been proposed to add it in the form of a solution in volatile solvents and as a suspension in water. The use of solutions, however, involves considerable losses of the solvent, and the use of suspensions or of the peroxide in the solid condition necessitates fine grinding which is difficult and expensive, and even with the finest grinding which is possible in practice, the limited amount of exposed surface of the peroxide is a handicap in the bleaching process.

It has now been found possible by using other peroxides than those hitherto proposed, to obtain a method which is technically practicable for bleaching flour, in which the chemical reagent does its work while present in the flour in the liquid condition, and by this means all drawbacks inherent in the use of solutions, suspensions or solid powders are obviated.

It has been found of considerable advantage to use organic peroxides liquid below 45° C., but mixtures giving to the flour a disagreeable odour are, of course, of no practical use.

According to the present invention, the bleaching of flour and other milling products is effected by mixing them with a small amount of one or more organic peroxides that give no bad odour to the flour, and for this purpose the reagent used is a liquid diaromatic peroxide which does not impart an objectionable odour to the flour, or is a liquid mixture of organic peroxides. The treatment is preferably followed by a simple mechanical or physical after-treatment or by both. In carrying out the new process, it is not necessary to melt the peroxide or the mixture before it is mixed with the flour. It can be brought to and kept in the liquid state after it has been mixed with the flour in the solid state by the addition of substances that lower the melting point or retard crystallization or both, and if necessary, moderately warming the mixture. Volatile organic substances are especially useful to this purpose.

The desired distribution of the reagent throughout the flour may be effected by spraying into the flour an emulsion of the liquid reagent in water with or without stabilizing colloids, ammonium salts, or organic nitrogen compounds of basic character, or by distributing throughout the flour a dry mixture of the liquid reagent with a mineral powder, such as kieselguhr, or a vegetable powder, such as rice starch, as has already been suggested for use with solid peroxides with a different object in view.

The novel method gives rise to an extremely uniform distribution of the reagent through the flour and a very great active surface of the reagent. The very intimate contact between the peroxide and the flour, however, does not give rise to any local deterioration of the flour grains, but in many cases it results in a saving of the reagent, or at least in a more rapid bleaching because the comparatively large free surface assists the decomposition of the peroxide.

The least practical method of bringing the reagent into the liquid state is by melting the pure organic peroxides which melt at low temperatures of about 40° C. and already proposed for the bleaching of flour, namely, di-acetyl peroxide, benzoyl-acetyl peroxide, and hydrocinnamyl peroxide which when in the pure state have properties which are unfavourable for bleaching flour.

In particular, the hydro-cinnamyl peroxide is out of the question owing to its intense and very objectionable odour. Although ortho-toluyl and meta-toluyl peroxides which melt at somewhat higher temperatures, about 55° C., may give some

trouble in actual practice, due to the tendency to sudden decomposition at melting temperature, they may nevertheless be used for the bleaching of flour in accordance with the present invention as they have the property of remaining easily in the super-cooled state after they have been melted, and particularly if they are absorbed by the flour while in the liquid condition.

Generally speaking, in order to liquefy peroxides below the temperature of 45° C., which is generally regarded as dangerous, the methods of lowering melting points known from general scientific principles may be employed; for example, the reciprocal lowering of melting points by the action of different peroxides one on the other or the lowering obtained by the addition of different substances in amounts of not more than from 10 to 30% or by both methods combined. The mixtures obtained are at a temperature of 20° C., or at least below 45° C., in the condition of a melt or of a super-cooled liquid. In order to lower the melting point in this way, substances such as low melting point solids may be used, for example, benzoyl anhydride, benzophenone, which are added to the peroxide in an amount not greater than that which gives an eutectic mixture.

Again, liquids may be used, for example in such an amount that the limit of miscibility is reached. In any event, the weight of the added material is always small relatively to the weight of the peroxide or peroxides, in contra-distinction to solutions in which the weight of peroxide is small relatively to the weight of the solvent, such as have been proposed for the bleaching of flour but are not found to be fit for the purpose in practice.

In carrying out the new method of bleaching flour, the asymmetrical aromatic peroxides give best results; they are liquid at low temperatures and can be easily supercooled. In particular, the liquefied products made in accordance with my co-pending application Serial No. 349,005 filed March 21, 1929, may be employed. These may be prepared to have any desired melting point, even as low as temperatures well below the normal room temperature.

The stability in the super-cooled state may be improved by adding to the mixture, or retaining in the mixture, related organic substances or decomposition products, even resinous substances such as benzaldehyde, benzo-phenone, or benzal-di-acetate. Even volatile substances may be used for lowering the melting point. They may leave behind in the flour after their whole or partial evaporation, a finely divided supercooled peroxide.

In some cases their vapour only suffices to render the peroxides deliquescent. Such bodies have the advantage that they have a low molecular weight, and therefore give a considerable lowering of the melting point for a relatively small addition by weight, and at the same time may act as a positive or a negative catalyst; such substances include acetic acid or pyridine. Again, they may have a favourable effect on the viscosity or the surface tension of the peroxide, as, for example, in the case of alcohols and ketones. An addition of such bodies assists the absorption of the liquid peroxide into the particles of flour. This absorption may sometimes be so slow, especially when the flour is wet, that extremely fine drops of the liquid peroxide remain in the flour.

There is no difficulty in adding the mixtures of peroxides described above to the flour; they may, for example, be injected from a fine spray. In any event, nothing more than moderate warming not exceeding 45° C. is necessary to ensure that the reagent will be present in the flour in the liquid state. The flour, after the liquid peroxide has been added, may be subjected to physical or mechanical after-treatment, as already proposed in the case of solid peroxides, or to energetic stirring for a shorter or longer period carried out in special apparatus to which heat is applied externally or generated by the friction in order to melt the peroxides or to make the bleaching more rapid.

On the other hand, this stirring may be carried out in ordinary mixing machines or flour apparatus. When the stirring is carried on for a long enough time, the liquid peroxide is completely absorbed in the flour particles, its surface is extremely extended, and all the advantages of the new method are fully obtained.

The advantages of the method described are generally speaking, ease of dosing into the flour, and easy uniform distribution without losing any amount of solvent, and in addition, generally speaking quicker bleaching or less chemical needed. Moreover, some peroxides which cannot be used in the pure state can be employed when admixed with others, even when in the pure state there is risk of explosion or of local intense action, as in the case of phenyl-acetic peroxide, or if they are liable to hydrolyze too easily, as in the case of benzoyl-acetyl peroxide. When used in liquid mixtures, however, their objectionable properties are moderated, but their oxidizing capability is added to that of the other constituents of the mixture. Some peroxides which in the pure state in the form of fine powder have little effect on the flour, become active when added to liquid mixtures; this is the case with para-toluyl peroxide. The cause of this may be that the organic acid formed from the peroxide during

bleaching does not accumulate at the surface of the particles of the peroxide, but is dissolved in the liquid reagent.

The following are examples of methods of keeping the peroxides in the liquid state at a low temperature or without danger of decomposition.

Example 1

Di-ortho-toluyl peroxide and di-meta-toluyl peroxide each alone has a melting point above 55° C. However, they yield an eutectic mixture melting at about 33° C. A mixture containing ortho toluyl peroxide, meta-toluyl peroxide and the asymmetric ortho-meta-toluyl peroxide, has an eutectic point below 20° C.

Example 2

A mixture of 12.5 grammes of benzoyl-acetyl peroxide, 7,5 grammes of di-ortho-toluyl peroxide, and 1 gramme of di-benzoyl peroxide melts at 26° C., while the eutectic point is some degrees lower still.

Example 3

A mixture of ortho toluyl-benzoyl peroxide with di-ortho-toluyl peroxide remains liquid below 20° C.

Example 4

Di-ortho-toluyl peroxide liquefies at temperatures lying below 40° C., when mixed with 10 to 30% of the following substances:—iso-propyl-alcohol, acetone, acetic acid, benzaldehyde, pyridine, phenyl-acetic acid, alone or in combination.

Example 5

Di-ortho-toluyl peroxide is stirred cautiously with 9 parts of dry rice starch at 55 to 60° C. until the mass has become a dry powder again. After cooling to room temperature, the peroxide is present in the liquid state but soaked up in the starch granules, as may be shown by inducing crystallization by the addition of a crystal of peroxide, as can be determined under the microscope.

All the melting points given should be regarded as approximate, because even for pure di-benzoyl peroxide as given in text-books and literature the melting point varies from 103.5 to 110° C.

The following are examples of methods of adding the liquid peroxide to flour:

Example 1

The mixture described under Example 1 above is sprayed while moderately heated in the desired amount directly into the flour to be treated.

Example 2

The mixture described under Example 2 above is emulsified in water to an amount of 2% to form a milky liquid. A very small amount of ammonium oleate is employed as a stabilizer and the mixture is sprayed into the flour in a Humphries apparatus. The mixture described in Example 2 above may again be mixed with a little water and oleic acid and stored for preparing emulsion with a large quantity of water and the calculated amount of ammonia at a later time.

Example 3

The mixture described under Example 3 above is mixed with 10% of acetone to make it more fluid, and is sprayed into the flour without heating.

Example 4

The powder obtained in accordance with Example 5 above is mixed with flour in a proportion of 1:4,000 parts.

The following are two examples of after-treatment after adding the peroxide to the flour.

Example 1

A liquid peroxide prepared in accordance with Examples 1 or 3 above is mixed with flour in a proportion of 1:40,000 in accordance with any of the above examples. The mixture is passed through agitating drums and mixing worms for some minutes. Inspection under the microscope shows that the peroxide is no longer present in the form of fine drops, but is soaked up into the flour particles. Also the colour reaction with Rothenfusser's reagent shows extremely uniform distribution of the peroxide.

Example 2

Flour is mixed with a small amount of a solidified mixture of meta-toluyl and ortho-toluyl peroxides and stirred at a temperature of 35° C. After some time the peroxide becomes soaked up into the flour in the liquid condition. Instead of heating the flour mixed with the peroxide, the mixture may be brought into contact with acetone vapour. After a certain amount of stirring, the peroxide becomes soaked up into the flour.

What I claim is:—

1. A method of bleaching flour and other milling products at a temperature not exceeding 45° C., which consists in mixing with the product to be treated a small amount of liquid organic non-dialiphatic peroxide, which does not contain hydro-cinnamyl peroxide and which does not solidfy at 45° C., and maintaining a bleaching temperature at which the peroxide remains in the liquid state.

2. A method of bleaching flour and other milling products at a temperature not exceeding 45° C., which consists in mixing

with a product to be bleached a small amount of liquid diaromatic peroxide, which does not contain hydro-cinnamyl peroxide and which does not solidify at 45° C. and maintaining a bleaching temperature at which the peroxide remains in the liquid state.

3. A method of bleaching flour and other milling products, which consists in mixing with the product to be treated at a temperature not exceeding 45° C. a small amount of liquid organic aromatic peroxide in a super-cooled state, and maintaining the mixture at a temperature not exceeding 45° C.

4. A method of bleaching flour and other milling products, which consists in mixing the product to be bleached at a temperature not exceeding 45° C., with a small amount of organic non-dialiphatic peroxide which does not contain hydro-cinnamyl peroxide, liquefying the peroxide after its addition to the flour at a temperature below 45° C. by means of a volatile organic substance, and maintaining the mixture at a temperature below 45° C.

5. A method of bleaching flour and other milling products at a temperature not exceeding 45° C., which consists in mixing with the product to be treated a small amount of liquid organic non-dialiphatic peroxide, which does not contain hydro-cinnamyl peroxide, and related organic substance having a low melting point, which is soluble in the peroxide in a quantity less than 50% of the peroxide and which will wholly dissolve in the liquid peroxide at a temperature below 45° C., and maintaining a bleaching temperature below 45° C. at which the peroxide remains in the liquid state.

6. A method of bleaching flour and other milling products at a temperature not exceeding 45° C., which consists in mixing with the product to be treated a small amount of liquid diaromatic peroxide, which does not contain hydro-cinnamyl peroxide, which does not solidify at 45° C., and a peroxide, which in pure condition is a solid substance below 45° C., in a quantity which will wholly dissolve into the liquid diaromatic peroxide at a temperature below 45° C., and maintaining a bleaching temperature below 45° C. at which the peroxide remains in the liquid state.

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