Patented Dec. 29, 1931 1,838,707

# UNITED STATES PATENT OFFICE

JOHN E. RUTZLER, JR., AND VAMAN R. KOKATNUR, OF ARLINGTON, AND PHILIP EDWARD ROLLHAUS, OF EAST ORANGE, NEW JERSEY, ASSIGNORS TO PILOT LABORATORY, INC., OF ARLINGTON, NEW JERSEY, A CORPORATION OF NEW JERSEY

## PROCESS OF AND COMPOSITION FOR BLEACHING OILS, FATS, AND WAXES AND THE PRODUCT RESULTING THEREFROM

No Drawing. Application filed April 9, 1928. Serial No. 268,789.

This invention relates to a process of and composition for bleaching oils, fats, waxes and the like, and to the product resulting from such bleaching process.

An important object of the invention is to provide a process of the character referred to by which oils, fats, waxes, greases, and the like may be more rapidly, efficiently, and completely bleached than by processes heretofore known.

Another object of the invention is to provide a process wherein peroxidized organic compounds are employed in bleaching oils, fats, waxes and the like at higher temperatures than heretofore could be successfully used, without the liberation of carbon dioxid from the peroxidized organic compounds.

Other objects and advantages of the invention will become apparent from the following description.

Organic peroxids, and notably benzoyl peroxid, have been employed heretofore for decolorizing oils, fats, waxes, resins, and the like and it has been found that the organic peroxids have certain advantages over other bleaching agents, particularly in that they are soluble to a certain extent in oils and fats, thus preventing emulsions, troublesome precipitates, and other troublesome factors in the bleaching process. However, the use of organic peroxids in prior processes has been attended with certain practical disadvantages. For example, most organic acyl peroxids decompose with the liberation of carbon dioxid upon heating to temperatures above 70° C. Some of the peroxids decompose with the liberation of carbon dioxid at lower temperatures. For example, benzoyl peroxid begins to evolve carbon dioxid at about 60° C. Moreover, it has been found that if benzoyl peroxid is heated in an oil to about 100° C. the decolorization effected, contrary to statements in the prior art, is less than when it is heated only to 60° C. In decolorizing crude cottonseed oil by this method, i. e. by heating the oil to about 100° C., the treated oil is not as light in color as prime summer yellow cottonseed oil.

We have discovered, however, that in the presence of strongly alkaline agents such as calcium hydroxid, peroxidized organic compounds can be heated to materially higher temperatures than heretofore has been possible without any substantial evolution of carbon dioxid. In the presence of such agents, instead of evolving carbon dioxid, the peroxidized organic compounds liberate oxygen, thereby considerably enhancing their decolorizing action. Alkaline agents and especially alkaline earth hydroxids have been found to be particularly suited for this purpose, since they not only prevent the undesirable pyrogenic decomposition of peroxids, but also bring down coloring matter by adsorption and by other means hereinafter described.

Heretofore it has been suggested that small amounts of organic peroxids will decolorize oils, fats, and waxes, when the temperature of the treatment is in the neighborhood of 100° C. However, Freer, Novy, Gelissen and others have shown and in our investigations we have found that at about 100° C. organic peroxides decompose with the evolution essentially of carbon dioxide. The decolorization of the oil or other material of like nature is due to the oxidation of certain coloring materials present. Thus it will be evident that if the peroxide decomposes without liberating more than a very small fraction of its available oxygen, its efficiency as a bleaching agent will be very low. In view of this fact it is evident that there can be but slight decolorization of any oil, fat, or wax at this temperature.

We have discovered that when a peroxid is heated in an oil in the presence of an alkaline agent and preferably an alkaline earth metal hydroxid such as calcium hydroxid, to approximately 100° C., instead of carbon dioxid being evolved, oxygen is largely liberated due to the induced pyro-oxygen decomposition of the peroxid. This discovery makes it possible, for the first time, to treat oils with organic peroxids at higher temperatures than formerly could be employed without impairing the bleaching efficiency of the peroxids. High temperature treatment may be desirable since at such temperature the reaction

velocities are considerably greater. Hence, better decolorization can be effected in a shorter time and with smaller amounts of the bleaching reagents.

Agents which induce the pyro-oxygen decomposition of the peroxids appear to have critical temperatures beyond which they do not so act. In the case of calcium hydroxid with benzoyl peroxid the critical temperature is in the neighborhood of 125° C. Thus, when a peroxidized organic compound is used in the presence of calcium hydroxid in the treatment of oils, fats, waxes and the like, the treatment may be conducted at temperatures in excess of 100° C. but below 125° C. without impairing the decolorizing efficiency of the peroxid.

Alkaline earth metal hydroxids which we prefer to employ in our bleaching process, together with peroxidized organic compounds have other desirable properties than that of preventing liberation of carbon dioxid from the peroxidized organic compound when high temperatures are used in the bleaching process. Even when employed at relatively low temperatures, alkaline earth metal hydroxids increase the reaction velocity of the pyro-oxygen decomposition of the peroxidized organic compound, thus effecting a quicker decolorization and permitting the use of smaller amounts of the reagents. Moreover, in the presence of moisture, they combine with free fatty acids, fatty acid anhydrides, and resinous materials which may be present in the substances treated with the result that they remove these materials and also coloring matters associated with them. In addition the alkaline earth metal hydroxids have the advantage that they remove coloring matter by adsorption.

Our process may advantageously be practiced in accordance with the following examples:

*Example 1*

About 4 kilograms of calcium hydroxid are placed in a large vessel provided with a suitable agitator and approximately 5 to 6 kilograms of water are added and the hydroxid well mixed therewith. About 100 kilograms of crude cottonseed or other oil which has previously been heated to about 70° C. is added during agitation to the mixture of calcium hydroxid and water. After agitating the mixture for several minutes approximately 0.4 of a kilogram to 1 kilogram of benzoyl-peroxid is added. Almost immediately the color of the mass deepens markedly. With further agitation the color of the mass becomes lighter. The mixture is then heated to about 90–95° C., agitated again for about 30 to 60 minutes and stored for settling. A good bleaching effect is noticeable almost immediately upon the completion of the treatment, although materially more decolorization takes place during storage.

*Example 2*

According to this example cottonseed or other oil is treated with an activated fatty acid peroxid, rather than with benzoyl peroxid, as in Example 1. All other conditions are kept the same as in Example 1.

*Example 3*

To 100 kilograms of molten grease, such as grease which has been recovered from slaughter house scrap and hotel and restaurant waste, 8 to 12 kilograms of calcium hydroxid, which has been thoroughly mixed with 10 to 15 liters of water, are added. To this mixture is added, with agitation, 1 to 2 kilograms of any organic peroxid, such for example, as benzoyl peroxid. An activated or plain peroxid may be used as desired. The mixture is then agitated for about 30 minutes, reheated to from 90 to 100° C., and stored. Even such recovered greases of the character referred to above can be satisfactorily decolorized by our process. The objectionable odor is changed to a fresh, sweet odor and even after months of standing the grease is found to keep well and to be practically free from rancidity.

If in the above treatments too great an amount of free fatty acid present in the grease or oil causes the formation of emulsions, due to the emulsifying action of the small amount of soap which is formed during the treatment, the process may be appropriately modified. For example, the oil may be partially neutralized before treatment by treating it with an alkaline agent in an amount sufficient to neutralize the oil to the desired degree.

*Example 4*

To 100 kilograms of molten beeswax or a solution of beeswax in any inert solvent such as solvent naphtha is added 9 to 14 kilograms of calcium hydroxid which has been thoroughly mixed with 9 to 16 liters of pure water. The mixture is heated to about 100° C., and agitated thoroughly. During agitation 1 to 2 kilograms of an activated fatty acid peroxid such as referred to above are added. The agitation is then continued for from 30 to 60 minutes. The solution is again heated to about 100° C., and stored for a week or more. The decolorization noticed after the treatment increases with time.

Instead of using the peroxidized organic compound and the alkaline earth metal hydroxid separately as described in the above examples, a suitable composition consisting essentially of the alkaline earth metal hydroxid and the peroxidized organic compound may be used. The deterioration of the strength of the peroxidized compound may be prevented by excluding moisture from the

composition at all times. Thus, either anhydrous calcium hydroxid, or calcium oxide, in suitable proportions may be intimately mixed with any anhydrous peroxidized compound, with or without the addition of fillers. Compounds containing water of crystallization and having a low vapor pressure are here construed as anhydrous, since such water of crystallization is not available for attack upon the peroxidized compound.

The result of treating an oil by our process is unexpected. For example, by treating crude cottonseed oil with benzoyl peroxid alone it is decolorized very little. The treated sample is scarcely distinguishable from a sample of the untreated oil. Similarly when crude cottonseed oil is treated only with calcium hydroxid and water, the resulting product is materially darker in color than the accepted standard of bleached cottonseed oil which is known to the trade as prime summer yellow. However, when the two reagents are used together the color of the product is very much lighter than the color of prime summer yellow cottonseed oil.

Colorimetric studies with a Campbell-Hurley colorimeter make it possible to express the foregoing results mathematically. Assuming that the crude cottonseed oil has a concentration of coloring matter equal to 250 units, and that prime summer yellow cottonseed oil has a concentration of coloring matter equal to 150 units, the treatment of the crude cottonseed oil with benzoyl peroxid alone in an amount equal to that employed in Example 1 gives a product having a concentration of coloring matter equal to not less than 220 units. If calcium hydroxid and water are used alone in amounts equal to those employed in Example 1, the product has a concentration of coloring matter of not less than 180 units. When, however, our preferred treatment is employed, the product has a concentration of coloring matter of only about 40 units.

From the foregoing it is obvious that upon the removal of 100 units of coloring matter from crude cottonseed oil, a product of the color of prime summer yellow cottonseed oil results. Our preferred process removes 210 units of coloring matter from the crude oil. If the crude cottonseed oil is treated with benzoyl peroxid alone, only 30 units of coloring matter are removed. Calcium hydroxid and water alone remove 70 units of coloring matter. The total number of units of coloring matter removed by the separate treatment of the oil with benzoyl peroxid and calcium hydroxid is therefore 100. By our process, we remove 210 units of coloring matter, or 110 per cent. more than the additive effect of benzoyl peroxid and calcium hydroxid when used separately. Since by our process we obtain an oil containing only 40 units of coloring matter in treating crude cottonseed oil, our product is almost 400 per cent. lighter in color than prime summer yellow cottonseed oil. The above results were obtained by testing oil which had been stored for two weeks after being bleached according to Example 1.

In order to produce more decolorization, in any case, more organic peroxid with an equivalent increase of alkaline earth hydroxid should be used. On the other hand, if the oil to be bleached is of the color of prime summer yellow cottonseed oil only about 0.2 of a kilogram of an organic peroxid and the alkaline earth hydroxid need be used. The bleached oil is found to be deodorized and sterilized, as well as decolorized. Thus, its keeping qualities are materially enhanced, and there is little tendency toward rancidity. Moreover, when the decolorization of the oil, fat, or wax is completed, filtration produces a crystal clear and practically ashless product.

While in our preferred examples, only two types of peroxids and three types of fatty materials are mentioned, it is to be understood that any fatty material or any suitable peroxidized organic material is within the scope of our invention. The amount of the peroxidized compound to be used depends, among other things, upon the nature and amount of the coloring matter present in the material to be decolorized and the amount of decolorization desired. Accordingly, a greater or lesser amount of the peroxidized material may be used. The invention is not limited to the quantities mentioned herein. Similarly, any other modification such as, the arrangement of steps, the amount of moisture to be used in the alkali, the physical conditions of the alkali, the amount of the alkali, the amount of the peroxidized material, the conditions of agitation, the temperature of treatment, etc., may be made as will be obvious to one skilled in the art. However, the amount of water used with the calcium hydroxid should not be more than 300 per cent. and the temperature of the treatment should not be substantially higher than the pyro-oxygen decomposition temperature of the peroxidized material used. Agitation, addition of moisture, and heating may simultaneously be effected by passing steam, at the temperature and pressure desired through the fatty material in the presence of the bleaching reagents.

By the term pyro-oxygen decomposition agent as employed herein is meant an agent which will promote the decomposition of a peroxidized organic acid at an elevated temperature with a substantial evolution of oxygen.

We claim:

1. The herein described process of treating oils, fats and waxes which comprises subject-

ing the material to be treated to the action of a peroxidized organic acid in the presence of a pyro-oxygen decomposition agent comprising a strong alkali.

2. The herein described process of treating oils, fats and waxes which comprises subjecting the material to be treated to the action of a peroxidized organic acid in the presence of an alkaline earth metal hydroxid.

3. The herein described process of treating oils, fats and waxes which comprises subjecting the material to be treated to the action of a peroxidized organic acid in the presence of calcium hydroxid.

4. The herein described process of treating oils, fats and waxes which comprises subjecting the material to be treated to the action of a peroxidized organic acid in the presence of a pyro-oxygen decomposition agent comprising a strong alkali at a temperature not substantially in excess of 125° C.

5. The herein described process of treating oils, fats and waxes which comprises subjecting the material to be treated to the action of a peroxidized organic acid in the presence of a moist alkaline earth metal hydroxid at a temperature of approximately from 60° C. to 125° C.

6. The herein described process of treating oils, fats and waxes which comprises subjecting the material to be treated to the action of an organic acyl peroxid in the presence of a pyro-oxygen decomposition agent comprising a strong alkali.

7. The herein described process of treating oils, fats and waxes which comprises subjecting the material to be treated to the action of benzoyl peroxid in the presence of a pyro-oxygen decomposition agent comprising a strong alkali.

8. The herein described process of treating oils, fats and waxes which comprises subjecting the material to be treated to the action of an organic acyl peroxid in the presence of an alkaline earth metal hydroxid.

9. The herein described process of treating oils, fats and waxes which comprises subjecting the material to be treated to the action of benzoyl peroxid and calcium hydroxid.

10. The herein described process of treating oils, fats and waxes which comprises subjecting the material to be treated to the action of a peroxidized organic acid in the presence of a pyro-oxygen decomposition agent comprising a strong alkali at a temperature below the critical pyro-oxygen decomposition temperature of the organic peroxid.

11. The process of decolorizing, deodorizing, and sterilizing cottonseed and other unsaturated oils, which comprises treating the oils with peroxidized organic acids in the presence of an alkaline earth hydroxid.

12. The herein described process of treating oils, fats and waxes which comprises heating the material to be treated, and treating the heated material with a peroxidized organic acid in the presence of a pyro-oxygen decomposition agent comprising a strong alkali at a temperature not substantially in excess of 125° C.

13. The process of decolorizing, deodorizing, and sterilizing cottonseed and other unsaturated oils which comprises treating the oils with an organic acyl peroxid in the presence of an alkaline earth metal oxid mixed with not more than 300 per cent. of water at a temperature not substantially in excess of 125° C.

14. The process of decolorizing, deodorizing, and sterilizing waxes which comprises treating a wax in liquid form with an organic acyl peroxid in the presence of moist calcium hydroxid at a temperature not materially in excess of 125° C.

15. The process of decolorizing, deodorizing, and sterilizing waxes which comprises treating molten wax with an organic acyl peroxid in the presence of moist calcium hydroxid at a temperature not in excess of the critical pyro-oxygen decomposition temperature of the peroxid.

16. A bleaching composition of the character described comprising a peroxidized organic acid, an alkaline earth metal oxid, and an adsorbent filler.

In testimony whereof we affix our signatures.

JOHN E. RUTZLER, JR.
VAMAN R. KOKATNUR.
PHILIP EDWARD ROLLHAUS.