The present invention relates to a process of refining oils and fats of vegetable and animal origin, and more particularly, to that portion of the refining process in which the oil is decolorized.

An object of my present invention is to provide a process of decolorizing oils and fats to produce a refined product of a particularly light color.

In addition it is particularly an object of my invention to provide a decolorizing process capable of affecting the more difficultly removable coloring matter in an oil, such as the carotenoid pigments.

A further object of my invention is the provision of a decolorization process that is simple and inexpensive in its operation, and which may be integrated readily with conventional methods of oil and fat refining.

The conventional method of refining oils and fats of vegetable and animal origin, hereinafter referred to as glyceride oils, includes the neutralization or removal or both of the various impurities such as free fatty acids, some of the coloring matter and gums. The fatty acids and gums, for the most part, are removable by conventional refining processes such as the neutralizing and precipitating action of caustic soda solution or other alkaline reagent. The color of the oil treated by such refining steps, in many cases, shows but a slight improvement, and it is necessary to treat the oil by other methods or with other materials, either before or after the treatment with alkaline reagents, to remove the coloring matter.

The coloring matter dissolved in the various glyceride oils which is most difficult to remove and which is not appreciably affected by alkaline reagents, comprises the so-called carotenoid pigments. It is the removal of this coloring matter of this type to which the present invention is primarily directed. The carotenoid pigments comprise primarily carotene associated with lycopene. They may also comprise pigments known as lutensins, lipochromes, lipoxanthins or chlorolipoids. These pigments include other polyene compounds, such as alcohol, ketones, and acids, and the entire class may be described generally as polyene pigments. They are naturally occurring pigments and are found widely distributed in both vegetable and animal material.

There are other coloring pigments associated with oils and fats, and to distinguish carotenoids from these other types of coloring materials, they may be defined more specifically as nitrogen-free polyene pigments consisting wholly or chiefly of a long acyclic chain of carbon atoms united in a sequence of conjugated bonds, which conjugations function as chromophore groups.

The carotenoid pigments vary in color from a bright yellow through a deep red or even a violet, to a dark blue, and it is believed that the depth of shade increases with the number of conjugations in consecutive union and decreases as the double bonds are saturated or otherwise eliminated.

The carotenoids are very susceptible to autoxidation in air, even at room temperature, so that they are decomposed with the formation of products of high molecular weight. Oil containing carotenoid pigments is improved in color upon subjecting it to a process of bleaching. Treatment of the carotenoid pigments may be accelerated by the application of heat, and heat bleaching of oils has become well known in the art. The process is not generally used, however, because the necessary high working temperatures have a deleterious effect upon the oil being treated. At lower processing temperatures the destruction of the carotenoids or their removal to improve the color of the oil is not complete enough for present day commercial standards.

It has also been proposed to use bleaching clay for the removal of carotenoid pigments, but this is an expensive process because an appreciable amount of the clay is required. The process is inconvenient because the clay must be removed by filtration. It also results in a considerable loss of oil through absorption of oil by the clay.

Palm oil is one of the glyceride oils that contains a relatively large amount of carotenoid pigments, and it is the decolorization of palm oil in accordance with my invention that produces the most striking results. The treatment of all glyceride oils is included in my invention, however, and oils such as cottonseed oil, sesame oil, soybean oil, kapok oil, peanut oil, lard, tallow and animal oils such as whale oil, may be treated by my process.

I have described my invention as applicable particularly to the removal of carotenoid pigments because these pigments are so difficult to remove by processes heretofore available, but my invention is not so limited and may be employed to remove other pigments if desired.

In accordance with the present invention, the reduction of the color in the oil is accomplished by the use of reducing agents effective for decolorizing oil. I have discovered that additions of a small amount of a starch, reduction of the above type to an oil will result in a marked reduction of the color of the oil. After completed
refining, the oil is in many cases practically void of color.

Suitable reducing agents that may be used in accordance with the present invention include those phosphorus compounds that comprise hypophosphorous acid (H₃PO₃) and its monobasic salts such as sodium hypophosphite (Na₂HPO₃). The relatively high activity of these compounds as reducing agents is well known in the art. It is not intended that other reducing agents of the type described shall be excluded from the scope of the present invention.

In practice, it is preferable that the decolorizing step utilizing the reducing agent be carried out prior to the usual refining operations with an alkaline reagent. In this manner, most of the products resulting from the reducing agent may be removed during the alkaline refining. Any remaining products are completely removed during the subsequent processing. For example, when hypophosphorous acid is used, there will be no trace of phosphorus compounds in the final product after conventional alkaline refining and subsequent treatments. In addition, the treatment with an alkaline reagent improves the color of the oil by further reducing any yellow color that may remain after treatment with the reducing agent, particularly the yellow pigments which are not acted upon as readily by the reducing agent as the red pigments.

As illustrated by the present invention, a reducing agent, such as hypophosphorous acid, in proportion of approximately from 1 to 1000, to 1 to 5000, is added to the oil heated to a desired bleaching temperature, preferably under vacuum. This may be done by adding the hypophosphorous acid to the oil in the treating tanks in a batch process, or by incorporating the acid as a step in a continuous process. Improved results are observed by agitating the oil during the treatment with the reducing agent. The remainder of the refining process remains unchanged from that in general commercial use.

The above described bleaching process, followed by a conventional refining operation, has resulted in the lowering of the color of rapeseed oil from 96 red and 3 yellow (1/3' column); soya bean oil from 94 red, 74 yellow and 5.6 blue, to 1.9 red, 30 yellow and 5.6 blue (3' column); Sumatra palm oil from 13 red, 75 yellow and 1.5 blue, to 1 red and 14 yellow (1" column); tallow from 23.8 red, 78 yellow and 4 blue to 6 red and 30 yellow (1" column), and African palm oil from 22 red and 70 yellow, to 1.5-2.3 red and 12-19 yellow (1" column).

In similar samples of tallow and African palm oil, which were treated by heat bleaching instead of the hypophosphorous acid bleach, the color was reduced only to 25 red, 75 yellow and 2 1/2 blue (1" column); and 2.4 red and 35 yellow (1" column), respectively. (All readings are on Lovibond scale.)

As an illustration of my invention when applied to a complete method of making an edible product, a crude Sumatra palm oil was heated to 235-255°C, at an absolute pressure of 10 mm. of mercury with the addition of hypophosphorous acid in proportion of one to two thousand. This temperature was maintained for approximately five to ten minutes, after which the oil was cooled to 70°C and then refined in accordance with a conventional refining process including agitation with sodium hydroxide solution, bleached with earth, filtered, hydrogenated, and deodorized. The final product exhibited a color reading on the Lovibond scale (5/4' column) of 1.0 red and 18 yellow.

As an additional illustration, a sample of crude palm oil, having a dark color, was treated with sodium hypophosphite in the proportion of 1 part to 80 dissolved in water and heated under a vacuum. Heating was continued until the water was removed, and then the temperature was raised gradually to 250°C which was maintained for approximately 5 minutes. The oil was then allowed to cool in a vacuum. A small amount of earth was added to insure a clear product. The finished oil exhibited a color reading of 1.4 red, 70 yellow (5/4' column). After a conventional alkaline refining treatment the oil had a color of 1 red, and 30 yellow (5/4' column).

The use of an elevated temperature greatly facilitates the bleaching action. Its use shortens the time required for the color removal and is preferable in a commercial operation. The most favorable temperature, hereinafter referred to as the bleaching temperature, at which the bleaching action takes place is subject to considerable variation dependent on the type of oil being refined. In the case of palm oil, which is high in color, the wax pigments may be removed as readily as possible to produce the best results. However, with peanut oil, the most favorable temperature was found to be approximately 165°C. As a general rule, there is no advantage in maintaining the oil at a high temperature for an extended period of time, and it is preferred that heating and cooling be accomplished as quickly as possible.

While it is not essential, the bleaching is preferably carried out under a vacuum of from 10 to 20 mm. of mercury pressure absolute, but the amount of vacuum has not been found to be critical. An atmosphere of inert gas may be employed to obturate or supplement the use of a vacuum.

The amount of reducing agent used will depend somewhat on the amount of coloring matter in the oil to be removed as well as on the conditions of operation, and may be varied over wide limits with satisfactory results. An excess does not accomplish any beneficial result. Quantities, to 1.3 red and 12 yellow (5/4' column); soybean oil from 94 red, 74 yellow and 5.6 blue (3' column); Sumatra palm oil from 13 red, 75 yellow and 1.5 blue, to 1 red and 14 yellow (1" column); tallow from 23.8 red, 78 yellow and 4 blue to 6 red and 30 yellow (1" column), and African palm oil from 22 red and 70 yellow, to 1.5-2.3 red and 12-19 yellow (1" column).

As a possible explanation of the bleaching action it is to be noted that the presence of a large number of double bonds or chromophore groups in carotenoid pigments is probably the cause of the color of the pigments, and it is possible that the action of the reducing agents comprises a destruction of the double bonds by saturating the same with hydrogen, or by separating the compound at such points. Such saturation or breaking of the double bonds may cause the color reduction herein described.

It is to be understood that the foregoing is given only as a possible explanation of the desirable results achieved by my invention, and it is not intended that any other explanation of the result of the chemical action involved is to be excluded.

The invention being thus described, it will be obvious that the same may be varied in many ways, such as variations in reducing agents, oils treated, and treating conditions. Such variations are not to be regarded as a departure from
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the essence of the invention and all such varia-
tions are intended to be included in the scope of
the following claims.

I claim:

1. In a process of refining glyceride oils, the
step of decolorizing the oil with a small amount of
a reducing phosphorous compound selected from
the group consisting of hypophosphorous acid and its
salts, while the oil is at an elevated
temperature and in a substantial absence of air.

2. In a process of refining glyceride oils, the
step of decolorizing the oil by treating it with
a small amount of a reducing phosphorous com-
 pound selected from the group consisting of
hypophosphorous acid and its salts while the oil
is at a bleaching temperature under vacuum.

3. In a process of refining glyceride oils, the
steps which comprise heating the oil to a bleach-
ing temperature under a high vacuum with a
small amount of a reducing phosphorous com-
 pound selected from the group consisting of
hypophosphorous acid and its salts, while the oil
is at a bleaching temperature under vacuum.

4. In a process of refining glyceride oils con-
taining an appreciable amount of carotenoid pig-
ments, the steps which comprise heating the oil
to a bleaching temperature under a high vacuum
with a small amount of a reducing phosphorous
compound selected from a group consisting of
hypophosphorous acid and its salts, and treating
the oil with an alkaline solution.

5. In a process of refining glyceride oils con-
taining an appreciable amount of carotenoid pig-
ments, the steps which comprise heating the oil
to a bleaching temperature under a high vacuum
with a small amount of a reducing phosphorous
compound selected from a group consisting of
hypophosphorous acid and its salts, cooling the
oil under a vacuum, and treating the oil with an
alkaline solution.

6. In a process of refining glyceride oils, the
step of decolorizing the oil by treating it with
a small amount of hypophosphorous acid at a
bleaching temperature under vacuum.

7. In a process of refining glyceride oils, the
step of decolorizing the oil by treating it with
a small amount of a salt of hypophosphorous
acid at a bleaching temperature under vacuum.

8. In a process of refining palm oil, the step
decolorizing the oil with a small amount of
hypophosphorous acid while the oil is at an ele-
vated temperature and in a substantial absence
of air.

9. In a process of refining palm oil, the step
decolorizing the oil by heating it with a small
amount of hypophosphorous acid at a bleaching
temperature under vacuum.

10. In a process of refining palm oil, the steps
decolorizing the oil by heating it with a small
amount of hypophosphorous acid at a bleaching
temperature under vacuum, and treating the oil
with an alkaline solution.

11. In a process of refining palm oil, the steps
decolorizing the oil by heating it with a small
amount of hypophosphorous acid at a bleaching
temperature under a vacuum, cooling the oil un-
der a vacuum, and treating the oil with an alka-
line refining agent.

12. In a process of refining palm oil, the steps
which comprise treating the oil with hypo-
phosphorous acid in a proportion of the order of
1 to 1000 and at a temperature of above 200° C.
under a high vacuum, cooling the oil under a
vacuum, treating the oil with an alkaline solu-
tion, and deodorizing the oil to produce an oil
having a particularly light color.

13. In a process of refining palm oil, contain-
ing an appreciable amount of carotenoid pig-
ments, the steps which comprise treating the oil
with hypophosphorous acid in a proportion of
the order of 1 to 1000 and at a temperature of
220 to 235° C. under a vacuum of less than 20
mm. of mercury, cooling the oil under vacuum,
treating the oil with a caustic solution to further
refine the same and remove phosphorous com-
pounds, washing the oil with water, and deodoriz-
ing the oil to produce a product having a par-
ticularly light color.

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