

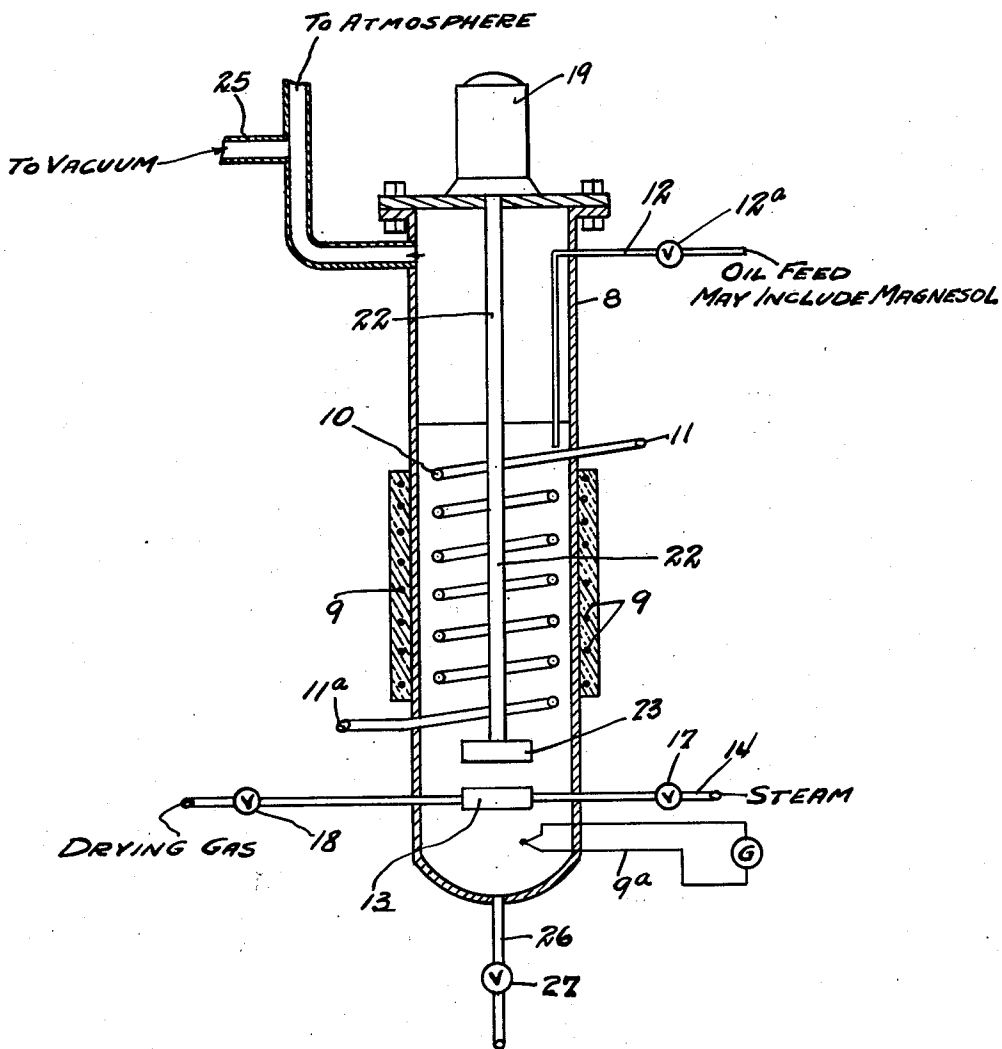
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ADSORBENT REFINING OF OILS

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## ADSORBENT REFINING OF OILS

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The present invention relates to a method of treating oils which are glycerides of higher fatty acids, and it has particular relation to the method of treating such oils for purposes of removing undesirable constituents, such as free fatty acids, coloring matter and break.

One object of the invention is to provide a process of treating glyceride oils whereby coloring matter, free fatty acids and break constituents can be reduced in amount or even eliminated with a minimum loss of oil.

A second object is to provide a process whereby break, free fatty acids and coloring matter in glyceride oils can be reduced or eliminated with a minimum loss of oil.

A third object is to provide a process of treating glyceride, drying oils or food oils to obtain products which, in the case of the drying oils, are suitable for cooking to provide varnishes or which, in the case of the food oils, are suitable for use in the preparation of salads or for other culinary uses, without subjecting the oils to alkali refining.

A fourth object is to provide a process of treating glyceride oils containing chlorophyll or other coloring agents which are hard to remove, whereby the content of these is reduced in a highly effective manner.

A fifth object of the invention is to provide a process of treating glyceride oils with refining adsorbents whereby a high degree of efficiency of the adsorbent agent is obtained.

A sixth object is to provide a process of treating glyceride oils with refining adsorbents, in which a minimum amount of the adsorbent is effective, to obtain an adequate degree of refining.

These and other objects of the invention will be apparent from consideration of the following specification and the appended claims.

It is well recognized that most of the glyceride oils, and especially the vegetable oils, are composed primarily of glycerides of a number of different fatty acids. However, they also include lesser amounts of other compounds or compositions, such as break constituents, free fatty acids and coloring matter. Many of these secondary components are objectionable in the oil, inasmuch as they often produce so-called "break," objectionable color, undue acidity, etc. The break constituents are especially objectionable in many operations, such as hydrogenation, and in the formation of alkyd resins due to the poisoning effect upon catalysts employed in the reactions involved.

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In order to refine the natural oils and thus to eliminate the objectionable constituents, various methods have heretofore been employed. For example, the oils have in many cases been subjected to treatment with alkali, whereby the break constituents and free fatty acids are removed or at least to a large extent removed. This technique is expensive because of the costs of materials and of apparatus employed in the operation. Also, excessive amounts of oil are converted into soaps and are removed as foots which are of substantially less value than the oil.

Another method of treating has involved steaming the oil under vacuum for purposes of reducing odor. The operation also successfully removes considerable amounts of free fatty acids and may be so conducted as to be especially effective in this respect.

Coloring matter usually is not completely eliminated by the foregoing operations, and in order to reduce the color of the oil it is often necessary to subject it to further treatment with adsorbent such as fuller's earth, acid activated clays and adsorbent carbons. To arrive at a product which is completely refined, that is, free of break, low in free fatty acids and of good color, numerous operations are thus required and very substantial amounts of oil are lost in the several steps.

In a co-pending application to Roger Christenson and Ralph Harpt, Serial No. 41,168; filed July 28, 1948, is disclosed an improved technique of treating glyceride oils in which the oils are admixed with a bleaching earth, such as fuller's earth, and while heated are subjected to the action of live steam at a temperature slightly above the boiling point of water, e. g. 110 to 130° C., and at atmospheric pressure for 10 minutes or more. The steam and the earth, acting simultaneously, effectively remove break constituents, greatly enhance color, and in many instances substantially reduce the free acid content of the oil. This process has been in successful operation for some time. It is advantageous inasmuch as the step of alkali refining the oil to remove break is often entirely avoided or, if it is required, in cases where the oil contains excessive amounts of free fatty acids or break, the amount of alkali required can be reduced to a minimum.

The present invention contemplates a process which in certain respects is similar to that disclosed in the above indicated application, but is distinguished therefrom by the employment of magnesium silicates and particularly of synthetic magnesium silicates as the adsorbent agents.

It has been found that the synthetic magne-

sium silicates possess certain substantial advantages over the adsorbents heretofore employed, inasmuch as they are substantially more active in important respects in the presence of steam than other adsorbing agents heretofore employed. For example, the amount of adsorbent employed can be materially reduced, thus lowering the cost of the operation. It would also follow that the filtering operation required to eliminate the adsorbent is facilitated since lesser amounts of material are to be removed from the oil. Furthermore, the volume of oil entrapped or entrained with the adsorbent agent is reduced.

Magnesium silicate, even without simultaneous applications of steam, tends to reduce phosphatidic break content. However, proper application of steam greatly accentuates this property. An oil inherently of moderate break content may be rendered break free by application of 3 to 6% of magnesium silicate without steam. However, this same oil when mixed with only 1 or 2% of magnesium silicates and then steamed by the technique herein disclosed will also be rendered break free.

The synthetic magnesium silicates are further characterized by a high capacity for the adsorption of acidic constituents contained in the oil, and their use as the adsorbent agent effectively reduces the free fatty acid content of the treated oil. Furthermore, the synthetic magnesium silicates are found to constitute excellent adsorbents of chlorophyll which is often a minor constituent of glyceride oils and which is very difficult to remove. The chlorophyll if allowed to remain in the oil tends to decompose to a certain extent and produce a type of discoloration which can only be removed by use of excessive amounts of decolorizing agents, if at all, in the conventional refining operations.

#### *The magnesium silicate component*

The synthetic magnesium silicates employed in the practice of the present invention are powders or fine granules and may be either hydrated or dehydrated. The preparation of such products which have adsorptive properties, permitting their use as decolorizing agents, has heretofore been described repeatedly in the patent literature as well as elsewhere. The silicates may, for example, be prepared by techniques such as are disclosed in U. S. Patents: No. 2,076,545, No. 2,163,525, No. 2,163,526, No. 2,163,527, No. 2,434,418, No. 2,450,549.

The silicates disclosed in these patents are to be regarded as merely representative of appropriate adsorbents for use in the practice of the invention. Numerous others are contemplated as being within the scope of the invention. One convenient material which is commercially available on the market is sold under the trade name of "Magnesol" by the Westvaco Chemical Division of Food Machinery and Chemical Corporation. Its composition is given as  $MgO \cdot 2.5 SiO_2 \cdot H_2O$ .

Other activated magnesium silicates of varying magnesia-silica ratios are contemplated as substitutes for this commercial material.

#### *Proportioning of magnesium silicates*

The magnesium silicates may be employed in varying proportions, dependent upon the activity of the specific magnesium silicate employed and also upon the characteristics of the oil to be treated and the degree to which refining is to be conducted. Oil containing excessive amounts

of one or more of the objectionable constituents of course will require larger amounts of the magnesium silicates than others of lower content. As a general rule, it may be stated that .2 to 5% by weight of magnesium silicate based upon the oil treated will be satisfactory. The most economical amount that will give a desired result can be determined in the laboratory by test runs on small samples.

#### *The oils to be treated*

The oils to be treated comprise any of the common glyceride oils, and notably the vegetable oils which are employed in the paint and food industries. These include linseed oil, soybean oil, cotton seed oil, corn oil, peanut oil and others.

These may be unrefined or partially refined. In the case of oils containing large amounts of break, e. g. soybean oil, partial refining, e. g. by water degumming, is advantageous and is usually employed. This operation is inexpensive and it materially reduces the amount of magnesium silicate required in the practice of the present invention by reducing the amount of gum to be removed. Water degumming is a familiar operation and is described in the text "Industrial Oil and Fat Products" by Alton E. Bailey, copyrighted in 1945 by the Interscience Publishers, Inc., New York, N. Y., pages 501-502 under the heading, "3. Refining by Hydration."

Usually the process of the present invention will be applied to an oil containing less than 0.25% of break in the form of phosphatides, proteins and the like. Soybean oils and other glyceride oils which have been fractionated or separated into portions of higher and lower iodine value by solvent fractionation methods, such as are disclosed in Freeman Patent 2,200,391, are very satisfactory for treatment in accordance with the provisions of the present invention. Either the raffinate oil or the extracted oil as obtained by such process may be treated in accordance with the present invention.

#### *Conditions of operation*

The equipment may be conventional deodorizing equipment such as is described by Bailey supra, Chapter XVIII, pages 534 to 557.

A glyceride oil containing one or more constituents such as break, color, or free fatty acids, e. g. soybean oil, cotton seed oil, linseed oil, or the like, or one of these oils which has been subjected to fractionation by means of solvents, or which has been water degummed, may be refined by admixing them with an active powder of synthetic magnesium silicate, such as "Magnesol," and heating, then steaming them in the apparatus at a temperature within a range of 200-250° F. The best results seem to be obtained within a temperature range of 210 or 212 to 225 or 230° F. If the oil is too cold, too much steam is condensed, and if it is too hot the break does not hydrate satisfactorily and is not so effectively eliminated or adsorbed by the magnesium silicate.

The steam at a temperature, for example, approximating that of the oil is preferably blown into the oil and distributed as uniformly as possible. To this end, it may be bubbled in through appropriate distributors disposed near the bottom of a container of oil. Agitators or other devices designed to effect more uniform distribution of steam and more thorough contact may be employed in the steaming operation.

The rate of adding steam may vary. If it is slow, a longer time will be required to effect thor-

ough treatment of the oil. If it is too fast, however, oil will be mechanically entrained in the vented vapors. A rate of approximately 0.005 pound to 0.20 pound of water as steam, per 100 pounds of oil may be bubbled through the oil per minute. If it is desired, the equivalent amount of water above specified may be pumped at the above stated rate to the hot oil, whereupon the water is changed into effective live steam.

The pressure in the system may be maintained at or near atmospheric in the container, but may be a few pounds lower, e. g. 2 or 3 pounds lower, or it may be somewhat higher, e. g. 8 or 10 pounds higher.

The period during which the oil containing the suspension of magnesium silicate is subjected to the action of live steam may vary considerably. The range may extend, for example, from approximately 10 minutes to 90 minutes or even several hours. The longer periods usually are not required and of course would be objectionable from the standpoint of economy. Usually, the completion of the steam treatment of the mixture of glyceride oil and magnesium silicate can be determined by simple tests, such as the conventional break test, in which a sample of the oil is subjected to heating to determine if break will separate out. The American Oil Chemists' Test, Official Method CA-10-40, is suitable for the purpose.

During the steaming operation, it is desirable to maintain a blanket of inert gas, such as carbon dioxide or nitrogen, over the body of oil undergoing treatment.

When the oil has been adequately treated, for example, until it is break negative as determined by the foregoing test, it is desirable to dry it in order to remove traces of moisture introduced by the steaming operation and to improve the color of the oil. This is conveniently effected by subjecting the oil to a blowing operation with an inert gas, such as carbon dioxide or nitrogen, which may be blown in until the oil ceases to cloud when a sample is cooled. Usually, the oil can be dried within a period of 10-30 minutes, but there is no objection to continuing the blowing operation with inert gas for longer periods of time, except perhaps because of the costs of conducting such operation. The temperature of blowing may be approximately 120° C. or higher, for example, up to 150° C. or thereabouts.

When the oil has been adequately dried, it may then be subjected to a filtering operation in a conventional filter press in order to remove the finely divided magnesium silicate suspended therein.

The oil as obtained by this treatment is break free. The acidity of the oil is usually greatly reduced and coloring matter, such as chlorophyll and the like, is also removed to a very large extent. This oil may, for many purposes, be entirely satisfactory without further treatment. It may, for example, be employed in alkyls or varnishes since it will cook into an alkyl without poisoning the catalysts or forming break. This oil may also be used as a salad or cooking oil or may be hydrogenated, without further treatment, to a solid fat. However, if it is desired to further reduce the free fatty acid content or to improve the color, additional treatments may be employed. These treatments are usually facilitated by reason of the prior treatment with magnesium silicate and simultaneously with live steam. The free fatty acid content can readily be improved without the application of alkali refining by subjecting the oil to a steaming operation, preferably under vac-

uum. This treatment may correspond to conventional deodorization or to refining with steam, which are well known in the art and may be extended to such extent as to remove nearly all of the free fatty acids, or at least to reduce them to a very small percentage. In event that the percentage of free fatty acids in the oil treated by use of magnesium silicate and steam is moderate, for example approximately .1 to 1.0%, it can be easily reduced to a value well below this point by steam deodorization or refining techniques.

Steam treatment of oil under vacuum is extensively discussed by Bailey supra, pages 531 to 557, inclusive. Essentially, the process involves bubbling through the oil live steam at a high temperature, e. g. 400 or 500° F., preferably under as high a vacuum as is feasible, e. g. .25 or .5 inch of mercury absolute pressure, until a low, free fatty acid content, e. g. .02% to .08%, is attained.

The use of partial alkali refining before or after steam-adsorbent refining is permissible and may prove advantageous but only in those cases where the initial acid value of the oil is extremely high.

The present invention contemplates as its basic feature the treatment of the glyceride oil simultaneously with magnesium silicate and live steam. However, there is nothing to preclude the incorporation of certain amounts of other adsorbent agents with the magnesium silicate. For example, the bleaching composition may include an adsorbent earth such as fuller's earth, or acid activated clay of the bentonite type with magnesium silicate. The use of activated carbons is not precluded but activated carbons tend to take up excessive amounts of oil and for this reason they are usually less desirable than the active earth such as fuller's earth, or activated clays such as acid activated bentonites, or the like. The proportion of the fuller's earth, acid activated clay or the like is susceptible of substantial variation in proportion. It may be employed in a range, for example, of .05 to 5% by weight based upon the oil treated, it may be employed additionally to the magnesium silicate, or it may replace a part, e. g. 10 to 75% by weight, of the magnesium silicate.

In the treatment of solvent-fractionated soya oil, the technique of the present invention is particularly advantageous. A raffinate oil obtained from degummed soya oil by the use of the Freeman procedure as disclosed in U. S. 2,200,391 represents a partially solvent-refined oil which is lower in iodine value, free fatty acids, and pigments than whole degummed soya oil, but is higher in break constituents than whole degummed soya oil. The use of the present invention, and in particular the use of a synthetic magnesium silicate and in conjunction with it a fuller's earth, results in an oil which is fully refined in that it is break negative with a free fatty acid content of below .08% and the color is equal to or lighter than alkali-refined, bleached soybean oil. Example VI on a subsequent page illustrates the treatment of such an oil with a mixture of adsorbents, one of which is a synthetic magnesium silicate.

It is characteristic of solvent fractionation by application of solvents such as furfural that the antioxidants or inhibitors of the oil are concentrated in the extract fraction. Therefore, the raffinates tend to be lower in such components than the original oil. This is often undesirable where the oils are to be employed for food purposes, e. g. as salad oils or for hydrogenation to form shortenings, because the oils, when exposed

to aging, may be subjected to oxidative rancidity and other forms of deterioration which are highly objectionable. In order to overcome these difficulties of the solvent extracted raffinates, it is desirable to incorporate anti-oxidants permissible in food products. One very convenient method of incorporating an anti-oxidant or inhibitor or combination thereof involves the addition of a certain amount of unrefined oil to the solvent extracted raffinate. For example, to a raffinate of soybean oil which is relatively low in tocopherol there may be added a certain amount of raw or degummed soybean oil or cottonseed oil or other oil containing inhibitor factors. A minor proportion of the raw or degummed oil will usually include an adequate amount of inhibitor factors to provide a product of sufficient stability for most purposes. The invention, for example, contemplates the incorporation of 5 to 25% or even higher percentages of the unrefined oil into the raffinate. Higher proportions of raw oil could be added but of course as the percentage increases the resultant blend or mixture tends to approach more and more the properties of a nonfractionated oil.

The technique of the present invention involving the simultaneous treatment of the oil with magnesium silicate and steam at the desired temperature and pressure is applicable to the raffinate either with or without blending with unrefined oil rich in inhibitors. If stability is not important, the raffinate to be treated need not include additions of anti-oxidants or anti-oxidant-bearing materials. The treatment with magnesium silicate and steam may be made directly to the raffinate. It is also contemplated to add the inhibitor, for example, in the form of unrefined oil or incompletely refined oil containing substantial amounts of inhibitor, before the refining operation. It is an important feature of the treatment with magnesium silicate and steam that inhibitors such as tocopherol are not appreciably affected in the oil by the treatment. Nearly all of the inhibitor factor remains undisturbed in the oil after treatment. Of course, synthetic inhibitors or anti-oxidants can be added to the raffinate from solvent fractionation. Such addition can be made either before or after refining of the oil with magnesium silicate and steam. In most instances, however, it is preferable to add the synthetic inhibitor or enrichments thereof to the oil after it has been refined with magnesium silicate and steam.

The use of a second adsorbent in conjunction with synthetic magnesium silicate is also particularly beneficial in the preparation of a light colored break negative oil from whole degummed soya oil. Such a procedure results in an oil meeting the requirements of a varnish-grade refined soya oil. Example II on a subsequent page illustrates this particular application.

It will be noted that the use of a secondary adsorbent of greater decolorizing strength than Magnesol results in a processed oil which is break negative and much lighter in color. In such treatment, one may consider the two adsorbents as complementing each other, with the synthetic magnesium silicate more or less selectively removing the break or phosphatidic constituents and the secondary adsorbent, such as fuller's earth or activated clays, removing greater amounts of pigments than the magnesium silicate alone would remove. The amount of the secondary adsorbent used is limited only by practical reasons of economy and the degree of

bleaching desired. It is entirely feasible to operate such treatment with combined adsorbents, and it is equally feasible to subject an oil to two separate and distinct treatments, the first being a contacting with the magnesium silicate and steam to remove break, with the second being a contacting with a fuller's earth or activated clay and steam to secure very light color.

It may be mentioned that in the best practice of the present invention, the use of a drying gas to effectively remove all water from the steaming is beneficial. Such drying is most effective when applied to the charge after the steam treatment has been completed and before the oil is filtered for removal of spent adsorbents. The drying results in further color improvement in that it removes water adsorbed by the magnesium silicate and secondary adsorbent, and makes available fresh adsorbing surfaces in the adsorbent. The filtration rate of a dry oil is also significantly better than that of a wet oil mixture.

#### Apparatus

In the practice of the invention, various embodiments of apparatus are suitable for conducting the treatment of an oil with steam in the presence of magnesium silicate. Such apparatus can conveniently be purchased from manufacturers of oil treating equipment.

For purposes of illustration is shown in the single figure of the drawing a simplified embodiment of apparatus.

This apparatus includes a container 8 which may be of any convenient material and of any shape or size. The container may, if desired, be heated by appropriate means, for example, by means of steam coils or by a steam jacket. However, for convenience of illustration, it is shown as being equipped with electrical heating elements 9. A thermocouple 9a may be provided for reading temperatures of the oil.

It should also be provided with appropriate cooling means to facilitate the cooling of the treated oil before it is filtered. Such cooling means may take the form of external heat exchangers, but for purposes of illustration is shown as a coil of tubing 10 with a connection 11 to a source (not shown) of cooling fluid, e. g. water, that can be circulated through the tube, and an outlet 11a to waste or to a refrigerator or other device designed to recool the fluid. Coil 10 can also be used for heating the oil by passing steam through 10.

Oil to be treated can be introduced into the container through conduit 12 with control valve 12a. The oil may be pre-mixed with the magnesium silicate or, of course, the latter material could be introduced into the oil already in the container by appropriate devices (not shown). The steam at desired temperature can be introduced into the oil through a distributor head indicated at 13 which is joined by conduit 14 to a source of steam (not shown). This same distributor may further be connected by conduit 16 to a source of inert drying gases, such as carbon dioxide or nitrogen or a mixture of the two, so that oil which has been steamed can be dried before it is cooled. Valves 17 and 18, in lines 14 and 16, permit the selection of steam or drying gas at will as the treating agent, and also permits the regulation of the rate of flow of these media.

To promote the distribution of the steam or the gas in the oil in the container, an agitator

mechanism is provided and includes a motor 19 disposed upon a head 21 for the container 8, and being provided with a shaft 22 extending down into the body of oil, and being provided with one or more impellers 23 designed thoroughly to agitate the oil and thus to promote its efficient contact with steam or drying gas. The space above the oil in the container should be high enough to accommodate for the bubbling and pitching of the oil while it is being blown with steam or gas. Preferably, it communicates with an outlet duct 24 which may discharge into the atmosphere. A branch 25 may lead to an appropriate source of vacuum. Valves (not shown) permit selection of the line or its branch as required. Usually the steam treatment of the oil containing the magnesium silicate will be conducted at or near atmospheric pressures, in which case any gases escaping may pass off to the atmosphere through the duct 24.

The oil containing magnesium silicate, e. g. .2 to 5% by weight or thereabouts, which has been blown with steam at atmospheric pressure until break is eliminated, can be dried by blowing it with carbon dioxide or nitrogen until a sample no longer produces a cloud when cooled. The oil can then be cooled to room temperature or somewhat above, by circulating cooling medium through coil 10. The cooled oil may be passed through a line 26, having valve 27, to a filter (not shown) where the magnesium silicate can be filtered off in any convenient manner.

If it is desired further to refine the oil in order to reduce the fatty acid content to even lower values, the oil, when filtered and free of magnesium silicate, may be returned to container 8 for further blowing with live steam. This time, the temperature of the oil may be around 400 or 500° F., e. g. about 475° F. Also, vacuum should be applied which is as high as is practicable. Preferably, it is of the order of 1 inch of mercury absolute pressure or much higher, e. g. 0.25 inch of mercury absolute pressure. The principles of steam deodorizing and refining are elaborated upon by Bailey supra, pages 534-557. They apply to treatment of an oil which has previously been treated by applicant's technique.

The deodorizing and refining can be continued until a desired acid value, as determined by conventional laboratory tests upon samples drawn off, is attained. This value practically always will be below .1% free fatty acid, and may extend down to .03 or .02%. As will appear later from certain examples, the use of large amounts of magnesium silicate in the steam bleaching operation will also produce oils of low acid value.

The oil refined with magnesium silicate and steam in container 8 can also be further bleached with adsorbent earths, or by heating the oil or by oxidation. Usually, deodorizing or steam refining is adequate to decolorize the oil. Heating the oil refined by magnesium silicate and steam to a temperature of about 500° F. or above will usually destroy heat labile pigments, which are the only ones remaining in the oil in substantial amount, and results in a product of excellent color.

In the industrial field, the use of magnesium silicate and steam preferably at atmospheric pressure has been found to be an advantageous method of preparing break free oils which can be cooked in the varnish kettle, bodied, or used to modify alkyd resins with or without further refining. Heretofore, in the preparation of oil

suitable for varnishes, it has been customary to subject the common soya oil or linseed oil to refining treatment, e. g. alkali refining, to remove break, then to a bleaching treatment to improve color. In accordance with the technique of the present invention, both of these steps can be accomplished simultaneously by subjecting the oil to bleaching by simultaneous application of magnesium silicate (preferably an amount of 1 to 3%) and steam at a moderate temperature and atmospheric pressure. The oil when so treated and subsequently dried and filtered may initially not be extremely light of color and may not be quite as low in color as oil refined by the conventional methods. However, in the cooking operations of kettle bodying or varnish making, most of the pigments which may remain in the oil after treatment with magnesium silicate and steam are readily destroyed to provide products which are fully as light in color as those obtained from conventionally alkali refined and bleached oils. The losses of oil in the treatment are quite comparable to those suffered in the conventional bleaching step alone. Therefore, an overall saving approximately equal to the conventional refining losses can be effected. With proper recovery equipment for the oil held in the spent adsorbent, the net oil loss in processing will be below 5%.

The following constitute specific examples illustrating the application of the invention to the preparation of a product designed particularly for use in paints and varnishes:

#### EXAMPLE I

In this example, a degummed soya oil was employed. In the degumming operation, the oil had been treated with water in order to remove a certain amount of break constituents. Such degumming operation is conventional and relatively inexpensive. The degummed oil, however, was still break positive. Degummed soya oil, in an amount of 1000 parts by weight, was introduced into an appropriate container, such as container 8, and heated to a temperature of 105 to 110° C. To the oil was added 12.5 parts by weight of magnesium silicate, namely "Magnesol" as above described. Enough inert gas was introduced to maintain a blanket above the oil, and steam was introduced through head 13 with vigorous agitation for a period of 30 minutes. The steam is generally introduced at a rate of 0.005 pound to 0.02 pound of water as steam per minute per 100 pounds of oil. In this experiment, the rate of steam introduction was .1333 pound of water as steam per minute per 100 pounds of oil. At the conclusion of this 30-minute steaming period, the oil was break negative. It was dried by bubbling inert gas through the conduit 16 for 30 minutes or until a sample of the oil tested free of moisture. The oil was then drawn off from the treating container, filtered and analyzed. The product was break negative. The free fatty acid content had been reduced from .29 to .15%.

The color of the oil was initially 11, based upon the Gardner scale, and the color of the treated product was 10.5 upon the same scale. This would seem to be a relatively small reduction of color. However, the color was reduced to a Gardner rating of 2.5 by heat bleaching at 550° F. in conventional manner. It would be practically impossible to heat bleach the oil to such low value had it not been subjected to

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the preliminary treatment with steam and adsorbent agent. The oil as obtained by the foregoing operations could be suitably used in the formulation of paints. It could readily be cooked into a varnish, or compounded into short or long oil alkyds. If desired, the oil could be steam refined under vacuum to provide a product of low acid value. Usually, such further refining is not required.

## EXAMPLE II

The oil employed in this example again was degummed soya oil which, however, contained some residual break as well as free fatty acids and cooling matter. In the refining operation, 1000 parts by weight of this oil were introduced into the container 8 along with 12.5 parts by weight of magnesium silicate, e. g. "Magnesol," and 7.5 parts by weight of an acid activated bleaching earth sold under the trade name of "Special Filtrol." This mixture was subjected to steaming as above described. Subsequently, the oil was dried, cooled and filtered. The oil had a greatly improved color, being of a Gardner value of 5.5. The free fatty acid value was .17 and the oil tested break negative. This example illustrates the simultaneous removal of break and orthodox bleaching effects as produced by acid activated bleaching earth incorporated into the oil along with the magnesium silicate. The product was break free and very light of color. These results were obtained in a single step. The losses were very low and yet the product was quite suitable for varnish cooking, heat bodying, or other operations involved in the preparation of paints and varnishes.

## EXAMPLE III

This example illustrates the application of the principles of the invention to the treatment of crude but partially degummed linseed oil. In the example, 1000 parts by weight of linseed oil admixed with 15 parts by weight of "Magnesol" was subjected to steam treatment in accordance with the conditions above specified in Example I. The steam treated oil was dried, cooled and filtered to provide a product which was break free. The free fatty acid was reduced by the treatment from an initial value of 1.15% to .95%. A slight reduction of color was simultaneously obtained. However, the product readily bleached upon heat treatment at 550° F. to a Gardner value of 5.5. The initial Gardner value was 11.

## EXAMPLE IV

In this example, partially degummed linseed oil corresponding to that described in Example III was subjected to the steam treatment in the presence of a mixture of magnesium silicate and acid activated clay. In the example, 1000 parts by weight of the oil were introduced into the container along with 15 parts by weight of Magnesol and 15 parts by weight of Special Filtrol. The steam treatment was conducted in accordance with the disclosure of Example I. The oil product as obtained was break negative, and had a Gardner color of 7. This Gardner value of course could be further reduced by application of heat as for example in bodying or cooking operations employed in making varnishes and alkyd resins.

## EXAMPLE V

In this example, the oil to be treated was a raffinate of soybean oil resulting from the ex-

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traction of degummed soya oil with furfural as a polar solvent. The oil in a proportion of 1,000 parts by weight was admixed with 15 parts by weight of a synthetic magnesium silicate, e. g. Magnesol, and the mixture was blown at 105 to 110° C. with live steam for a period of 30 minutes, as described in Example I. The oil was initially break positive, had a fatty acid content of .037% and was of a Lovibond color of 50Y;7R. This oil, when treated with magnesium silicate and steam under the conditions above specified, yielded a product which upon drying and filtering was break negative, of a fatty acid content of .014 and of a Lovibond color of 30Y;5R. A portion of this product was steam deodorized under vacuum in accordance with conventional technique. After deodorization, the color of the oil was 5Y;0.5R (Lovibond) and the free fatty acid content was below 0.025%. A second portion of the refined oil was hydrogenated to an iodine value of 70, and was then steam deodorized under vacuum according to conventional techniques. The resulting hardened oil had a Lovibond color of 3Y;0.3R and the free fatty acid content was below 0.025%.

## EXAMPLE VI

According to this example, 1000 parts by weight of a raffinate of soya oil which had been obtained by fractionation of soya oil with furfural and which contained a small amount of break, coloring matter and free fatty acids was admixed with 15 parts by weight of fuller's earth and 15 parts by weight of synthetic magnesium silicate. It was then treated with live steam in accordance with the provisions of the preceding examples. The oil initially contained .043% of free fatty acids and was of a Lovibond color of 50Y;6.5R. Of course, as above stated, the oil was break positive. After treatment with live steam under the conditions specified, followed by drying and filtering, the oil was break negative, of a free fatty acid content of .013, and had a Lovibond color of 7Y;0.6R. Without further treatment, this oil could be deodorized to a salad or cooking oil; hydrogenated and deodorized to a shortening or margarine stock; or could be used in alkyd or varnish preparation.

## EXAMPLE VII

In this example, 1000 parts by weight of vegetable oil, consisting of 85% by weight of a raffinate of soya oil which had been obtained by fractionation of a degummed soya oil with furfural and 15% by weight of whole degummed soya oil, was admixed with 20 parts by weight of synthetic magnesium silicate, e. g. "Magnesol." It was then treated with live steam in accordance with the provisions of the preceding examples. The oil initially contained 0.15% by weight of free fatty acids, was of a Lovibond color of 60Y;8.0R, and the break test was positive. After the oil was treated as above specified, it was dried and filtered. The final oil, upon analysis, was break negative with a free fatty acid content of .04% and a Lovibond color of 35Y;1.8R.

The above refined oil was hydrogenated to an iodine value of 70, and was then steam deodorized under vacuum to yield a hardened product with a Lovibond color of 4Y;0.4R. The Swift stability (active oxygen method) of the hardened product was 120 hours.

## EXAMPLE VIII

In this example, 1000 parts by weight of vege-

table oil having the same composition as that used in Example VII was admixed with 20 parts by weight of synthetic magnesium silicate, e. g. "Magnesol," and 15 parts by weight of fuller's earth. It was then treated with live steam in accordance with the provisions of the preceding examples. The oil initially contained 0.14% by weight of free fatty acids, was of a Lovibond color of 60Y;3.0R, and was break positive. After the oil was treated as above specified, it was dried and filtered. The final oil, upon analysis, was break negative and had a free fatty acid content of .045% and a Lovibond color of 12Y;1.0R.

The above refined oil was hydrogenated to an iodine value of 70, and was then steam deodorized under vacuum to yield a hardened product with a Lovibond color of 4Y;0.3R. The Swift stability (active oxygen method) of the hardened product was 120 hours.

#### EXAMPLE IX

In this example, 1000 parts by weight of a degummed soya oil was admixed with 15 parts by weight of a synthetic magnesium silicate, e. g. "Magnesol," and treated as specified in Example I. The oil initially contained 0.28% by weight of free fatty acids, was break positive and had a Lovibond color of 70Y;15R. The dried and filtered refined oil was break negative, had a Lovibond color of 30Y;6R, and contained 0.20% free fatty acid.

A portion of this refined oil was steam deodorized under vacuum in accordance with conventional technique. After deodorization, the color of the oil was 4Y; 4R Lovibond, and the free fatty acid content was 0.046% by weight.

As a means of comparison, a portion of the original degummed soya oil was alkali refined and deodorized in accordance with conventional techniques. This final deodorized oil had a Lovibond color of 15Y;1.5R, and a free fatty acid content of 0.020%. The refined oil produced, therefore, by the present invention has been shown to yield a deodorized oil with lighter color than one produced from alkali refining.

A second portion of the oil refined with synthetic magnesium silicate as specified above was hydrogenated to an iodine value of 70, and then steam deodorized under vacuum by conventional technique. The hardened deodorized oil had a Lovibond color of 3Y;3R, and a free fatty acid content of .058%. A sample of the alkali refined oil previously prepared was similarly hydrogenated and deodorized to yield a product with a Lovibond color of 13Y;1.2R and a free fatty acid content of 0.020% by weight.

The same alkali refined oil was also given a conventional bleach with 1% of acid activated clay, before hydrogenation. After deodorization, this hardened deodorized product had a Lovibond color of 4Y;4R, and a free fatty acid content of 0.030% by weight. This data demonstrates that the refining by means of synthetic magnesium silicate as described above produces an oil which can be processed to a hydrogenated and deodorized product equal to or superior to one which is alkali refined and bleached by conventional techniques.

The oil used in the above series of experiments could also have been prepared as specified in Example II.

The several embodiments of the invention herein disclosed are by way of example. It will be apparent that numerous modifications may be made therein without departure from the spirit

of the invention or the scope of the appended claims.

I claim:

1. In a process of refining glyceride oil containing color matter, the steps of admixing the oil with synthetic magnesium silicate having active adsorbing surfaces, then blowing the oil at 200 to 250° F. with live steam to adsorb the coloring matter upon the magnesium silicate, and filtering off the magnesium silicate with the adsorbed coloring matter.

2. In a process of refining glyceride oils containing chlorophyll as a coloring matter, the steps of admixing the oil with magnesium silicate having active adsorbing surfaces, then blowing the oil at 200 to 250° F. with live steam to adsorb the chlorophyll upon the magnesium silicate, cooling the oil, and filtering off the magnesium silicate with the adsorbed chlorophyll.

3. In a process of refining glyceride oils containing break, the steps of admixing the oil with magnesium silicate having active surfaces adapted to adsorb the break, then blowing the oil at 200 to 250° F. with live steam to adsorb the break upon the active surfaces, and filtering off the magnesium silicate with the adsorbed break.

4. In a process of refining glyceride oils containing free fatty acids, the steps of admixing the oil with magnesium silicate having active adsorbing surfaces, then blowing the oil at 200 to 250° F. with live steam whereby to adsorb selectively the free fatty acids upon the surfaces, cooling the oil, and filtering off the magnesium silicate with the adsorbed free fatty acids thereupon.

5. In a process of refining glyceride oils containing coloring matter, break, and free fatty acids, the steps of mixing the oils with adsorbent magnesium silicate having active adsorbing surfaces, then blowing the oil for 10 to 90 minutes with live steam at a rate of .005 to .2 pound per minute and at a temperature within a range of 200 to 250° F. to adsorb the coloring matter, break, and free fatty acids from the surfaces, cooling the oil, and removing the magnesium silicate.

6. In a process of refining glyceride oils containing break, the steps of admixing the oil with .2 to 5% by weight of magnesium silicate having active adsorbing surfaces, then blowing the oil with live steam at a temperature within a range of 210-230° F. for a period of 10-90 minutes, drying the oil by blowing it with inert gas, cooling the oil, and filtering off the magnesium silicate to obtain a break-free product.

7. A process as defined in claim 6 in which the product free of break is subjected further to a refining operation to remove free fatty acids.

8. A process of refining glyceride oils containing break, the steps of admixing the oil with .2 to 5% by weight of magnesium silicate having active adsorbing surfaces, then blowing the oil with live steam at a temperature within a range of 210 to 230° F. and at a pressure approximately atmospheric for a period of 10 to 90 minutes, then drying the oil, and filtering the magnesium silicate therefrom.

9. A process as defined in claim 8 in which the oil treated is degummed soya oil.

10. A process of treating a glyceride oil suitable for food and containing break, free fatty acids and coloring matter, which process comprises admixing the oil with .2 to 5% by weight of magnesium silicate having active adsorbing surfaces, then blowing the oil with live steam at a temperature within a range of 210 to 230° and at



approximately atmospheric pressure for a period of 10 to 90 minutes, drying the oil by blowing it with inert gas, cooling the oil and filtering off the magnesium silicate to obtain a break free product, then refining the oil by blowing it with live steam under vacuum to reduce color and free fatty acid content.

11. A process as defined in claim 10 in which the oil treated is soybean oil.

12. The method of preparing a break free glyceride oil of low color and low fatty acid content, which method comprises subjecting a raffinate fraction of glyceride oil, obtained by fractionating with furfural a glyceride oil which comprises a mixture of highly unsaturated glycerides and less highly unsaturated glycerides, to live steam at atmospheric pressure in the presence of magnesium silicate.

13. In the method of preparing a glyceride oil product which is break-free, low in color and free fatty acids but good in resistance to oxidation, from a raffinate low in tocopherol resulting from the solvent fractionation of a glyceride oil with furfural, the steps which comprise admixing the raffinate with unfractionated oil of relatively higher tocopherol content, adding .5 to 5% by weight of magnesium silicate to the mixture, blowing the mixture with live steam at atmospheric pressure and at a temperature of 210 to 230° F. for 10 to 90 minutes, drying and cooling the mixture, and filtering off the magnesium silicate to provide said product.

14. The steps as defined in claim 13 in which the oil of relatively higher tocopherol content is soybean oil.

15. A process as defined in claim 1 in which the oil treated is of a class consisting of soybean oil, linseed oil, and raffinate soybean oil from the extraction of soybean oil with a polar solvent.

16. In a process of bleaching a glyceride oil, the steps of introducing a mixture of synthetic magnesium silicate and acid activated clay into the oil and blowing the oil at a temperature of 210 to 230° F. with live steam to effect adsorption of coloring matter from the oil, then removing the mixture.

17. The steps as defined in claim 16 in which

the oil is of a class consisting of soybean oil, linseed oil, and raffinate oil from the extraction of soybean oil with a polar solvent.

18. In a process of bleaching a glyceride oil, the steps of blowing said oil in the presence of a mixture of adsorptive magnesium silicate and fuller's earth, and at a temperature of 210 to 230° F. to effect color adsorption, then removing the mixture from the oil.

19. In a process of preparing bleached oil of relatively high stability, the steps of blowing with live steam a mixture of soybean raffinate oil from solvent fractionation of soybean oil, and degummed soybean oil, the mixture being at a temperature of 210 to 230° F., and the blowing operation being effected in the presence of a mixture of adsorptive magnesium silicate and fuller's earth.

20. The steps as defined in claim 1 in which the mixture of oil and magnesium silicate is further mechanically agitated while being blown, in order to effect thorough contact of the steam with the oil and the magnesium silicate.

21. The steps as defined in claim 2 in which the mixture is further mechanically agitated while being blown in order to effect thorough contact of the steam with the oil and the magnesium silicate.

22. The steps as defined in claim 5 in which the mixture of oil and magnesium silicate is further mechanically agitated while being blown with steam, in order to effect thorough contact of the steam with the oil and magnesium silicate.

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