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PROCESS OF TREATING GLYCERIDE OILS WITH ACTIVATED MAGNESIUM OXIDE

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The present invention relates to the refining of edible oils. More specifically, it pertains to the treatment of edible glyceride oils, having particular reference to improvements whereby reversion characteristics of such oils, as well as rancidity characteristics, are prevented, and the provision of a non-revertible, non-rancid oil, and process for producing the same, is a principal object of the invention.

More specifically, it is an object of the invention to remove from glyceride oils, such as soybean oils, or the like, the impurity, or impurities, causing reversion characteristics to develop therein by subjecting such oils to thorough mixing with activated magnesium oxide.

Yet more specifically, it is an object of the invention to treat crude or purified edible glyceride oils, such as soybean oils, or the like, with activated magnesium oxide and with activated carbon thereby to prevent the development of reversion characteristics as well as rancidity characteristics and to produce an edible oil therefrom which will not revert or become rancid even when stored for prolonged periods of time.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

Present methods of refining edible glyceride oils are well known and need no elaboration in detail. Briefly, however, the steps generally involved consist of neutralization in which the oil is emulsified with caustic soda solution and after the emulsion breaks the oil is separated. It is then washed and dried. Thereafter it is bleached by means of small amounts of suitable adsorbents and preferably winterized. The final step is one of deodorization. Preferably, before and in conjunction with the deodorization step, however, the improvement of the present invention is practiced, although a purified oil up to this point can be substituted by a more or less crude oil as will more fully appear hereinafter.

The refining process briefly outlined above has for its objective the removal of the undesirable accessory substances in the crude oil. The neutralization and washing steps remove free fatty acids, phosphatides, sterol glucosides, some of the sterols, gums, and most of the nitrogenous compounds. Bleaching removes a considerable part of the color pigments and probably some colorless substances as well. During winterization, which in the case of soybean oil is unnecessary for the purpose of removing saturated glycerides or stearines, a small quantity of insoluble material of unknown structure, possibly

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a wax or sterol, separates and is removed by winter-pressing. During deodorization, practically all impurities which are volatile in steam at low pressures are removed.

Freshly refined soybean oil made from a crude oil derived from high grade beans has a characteristic odor but is bland and sweet. It can be considered to be a high-class salad oil since the characteristic odor is not objectionable. However, when heated to 425° F. in a so-called "cooking test," a sharp, "grassy" odor develops. The chief drawback of refined soybean oil, however, is that in the course of from a few days to months, depending upon conditions, the oil undergoes a peculiar change which is known as "reversion." This deterioration is accompanied by the development of an undesirable odor and flavor which has been variously described as "cucumbery," "grassy," "painty," or "fishy." There is undoubtedly a progressive change in odor and flavor, and the odor is not the same at the beginning of the reversion period as toward the end. The process is not true odor reversion because the odor does not revert to that of either the crude oil or the deodorized oil.

It should be observed that reversion and oxidative rancidity are different, although possibly related, phenomena. Corn oil, one of the best food oils, causes little trouble because of reversion but becomes rancid more rapidly than soybean oil as measured by peroxide formation. Attempts to correlate soybean oil reversion with peroxide values have not led to fruitful results.

A tremendous amount of research effort has been expended in attempting to prevent soybean oil reversion and to determine the underlying cause. The theory that has attracted the largest following in recent years is that soybean oil reversion is due to the presence of a small percentage of linolenic acid, an unsaturated fatty acid containing three double bonds, in the glyceride molecules. Corn and cottonseed oil, which are not subject to much reversion, do not contain a detectable amount of linolenic acid. On the other hand, linseed oil which contains a high percentage of linolenic acid is characterized by a typical, strong "painty" odor. According to this theory, the linoleic acid decomposes in storage to odoriferous substances because of oxidation with air, condensation, ring closure, or some unknown kind of reaction.

On this assumption work on the reversion problem has been directed toward the elimination of linolenic acid. Since it is impractical in

this case to remove the linolenic acid by hydrolysis of the glycerides and separation of the fatty acids, the main line of attack has been partially and selectively to hydrogenate the oil with the objective of converting the linolenic acid to a more saturated acid such as linoleic. Unfortunately, the partial hydrogenation has not been amenable to selective control with the result that stearines and solid isomeric unsaturated acids are formed to an undesirable extent. Furthermore, reversion is not entirely prevented and the oil acquires in addition a "gassy" odor.

It would seem that reversion is due to the presence of minute quantities of impurities or accessory substances that have not been removed in the refining process. In particular, nitrogenous impurities, like phosphatides or fragments thereof, slowly decompose on standing to yield amines having a penetrating and objectionable odor. The fact that refined soybean oil made from first grade beans is more stable than that made from beans containing frost and field-damaged beans indicates that reversion may be caused by residual impurities in the refined oil. These impurities cannot completely be removed by conventional refining methods.

The invention herein disclosed was, in effect, the accidental outgrowth of a fundamental study on the chromatographic adsorption of the colored accessory compounds in soybean oil. In this work soybean oil dissolved in hexane was passed through a glass column uniformly packed with a light-colored adsorbent agent. When using magnesium oxide as the adsorbent material, the colored materials in the oil were selectively adsorbed. The most strongly adsorbed pigment was adsorbed first, the next strongly adsorbed material was then adsorbed and so on, until, at the end of the pass, the adsorbent material was colored by a series of bands of pigments of different colors. Each band represented a different pigment or mixture of pigments. The bands were spread apart and the edges sharpened by passing more solvent through the column. Then, by pushing out the column material, the bands were separated mechanically and the adsorbed material in each band studied separately. It was seen that magnesium oxide had adsorbed green chlorophyll more strongly than the yellow and red pigments. All of the green pigment formed a tight green band at the top of the column.

The green band adsorbed on magnesium oxide was removed from the column and the adsorbed material extracted with solvents. It gave a positive test for chlorophyll. After removal of solvents it was noted that the greasy residue had a strong, unpleasant odor, resembling that of a badly reverted soybean oil. An impurity responsible for the reversion of soybean oil was thus removed by the magnesium oxide. The oil passed through the magnesia column was then treated to remove solvent and stored in corked glass bottles in diffused daylight for a long period of time. It did not revert.

It later was developed that a solvent such as hexane was unnecessary and that the oil could be effectively treated simply by agitating with the proper amount of activated magnesia under suitable conditions, and then filtering off the magnesia.

The effectiveness of this treatment depends upon the removal by selective adsorption on the magnesia of some impurity or impurities which cause reversion. By the present invention substances apparently are removed which directly decompose or oxidize to products having disagreeable odors and flavors, or substances having a catalytic effect on the decomposition of otherwise stable accessory substances, or unsaturated glyceride molecules are removed. The chlorophyll substances also may be the cause of reversion, or the revertible substances may be removed simultaneously with the chlorophyll. In any event, the impurities, or those substances responsible for the reversion characteristics, were removed with the removal of the chlorophyll.

In practicing the present invention the following controlled operating conditions cover preferred operating ranges for treating a glyceride oil with activated magnesium oxide:

Temperature	20–150° C. (preferred 40 to 60° C.)
Time	2–4 hours
Quantity of MgO	0.1 to 6.0% (based on oil)
Pressure	Normal or sub-atmospheric

Any temperature up to 150° C. gives acceptable results. Above 150° C. some discoloration of the oil occurs and the oil is liable to oxidation. Since the selectivity of the adsorption on magnesia is not increased by higher temperatures and is just as effective at ordinary temperatures, it is preferable to work in a range of 40 to 60° C.

The time of treatment is not independent of the other factors but is partially dependent upon the quality of the starting oil and the quantity and activity of the magnesia used. A treatment period of from 2 to 4 hours is preferred.

The quantity of magnesia to be used also is not an independent variable but depends on the activity of the magnesia and the kind of starting oil. When starting with an alkali-neutralized, washed, dried, bleached and winterized oil, only about 0.5 per cent of an activated magnesia is required. When starting with a neutralized, washed and dried oil of the same stock, from 2.5 to 3 percent of the same grade of magnesia is required for effective treatment. In treating an oil having a greater tendency to revert than soybean oil, such as linseed oil, it is necessary to use a larger amount of magnesia, in the range of from 3 to 6 per cent. Oils such as cottonseed and corn which are subject to but little reversion, can be treated effectively with quantities of magnesia down to 0.1 per cent.

Preferably sub-atmospheric pressure is used, for example, in the range of 20 to 50 mm. Hg. The vacuum assists in de-aerating the magnesium and protects the oil from oxygen of the air.

During the treatment of the oil with magnesia, it is best to agitate the mixture thoroughly in order to obtain intimate contact between the oil and the finely divided adsorbent agent.

Either a powdered or granular type of activated magnesia can be used. Pelleted, activated magnesia from the powder would be acceptable. A granular or pelleted form of magnesium oxide is preferred because of ease of filtration.

Ordinary magnesium oxide purchased on the market is inactive and does not have any selective adsorption properties. However, the same material can be activated by heating with water to about 100° C., for approximately one hour, filtering, drying and heating in the range of 350° to 500° C. for 3 hours or longer. Commercial products also are available.

Preferably, the oil is put through the initial steps of the conventional refining process which includes alkali-neutralization, washing and dry-

ing. In certain cases it may be advantageous to start with crude oil and employ a larger quantity of magnesia, but in most cases it is better partially to purify the oil before treatment. In case the crude oil is particularly poor in quality, the best results are obtained by bleaching the oil in the regular manner with bleaching earths before treating with magnesia. Although deodorized oil may be used, it is preferable to follow the magnesia treatment with the deodorization step.

The magnesia treatment of the present invention is applicable to all types of revertible glyceride oils including vegetable, animal and marine oils. As an extreme example, linseed oil which is but seldom used for edible purpose, can be rendered sweet and non-reverting by the magnesia treatment when followed by deodorization. Fish oils, such as sardine and pilchard oils, are remarkably improved so far as odor and flavor are concerned.

Example 1

The magnesia treatment was carried out in a vacuum-tight steel vessel equipped with heating and cooling coils and a two-bladed agitator. Additional equipment included plate and frame presses, storage and transfer tanks, pumps and a deodorizer.

One barrel of neutralized, washed, dried and bleached soybean oil, 418 lbs., was pumped into the vessel and to this was added 2.1 lbs. (0.5 per cent) of magnesia. The stirrer was started and the vessel evacuated to about 20 mm. Hg pressure. The oil was warmed to about 48° C. and stirred for 3 hours. The charge was then pumped to a tank and mixed with 2 gallons of filter aid. The oil was then pumped to a filter press and filtered through paper, recycling until the filtrate was clean. The filtered oil was then pumped to the deodorizer and treated with steam under high vacuum under conditions identical with those used in making ordinary edible soybean oil.

The finished oil was clear yellow in appearance. On the Lovibond scale the color was 20Y–2.3R. The flavor was extremely bland and sweet. It had a very faint, pleasant odor. Particularly noteworthy was the odor when the oil was heated to 426° F. in the "cooking" test. The strong, grassy odor of soybean oil did not evolve although a faint sharp odor could be detected.

Example 2

A sample of crude linseed oil was neutralized, washed and dried by the process similar to that used for soybean oil. It was then treated with 5.6 per cent of active magnesium oxide at 55° C. for 3 hours. The magnesia was filtered off and the oil deodorized by vacuum steam distillation in the regular manner. The resulting oil was free of "fishy" or "painty" odors and remained that way upon storage.

By means of the present invention a tremendously increased supply of high grade edible oil can be made available from domestic sources. Soybean oil in quantity now can be refined to a palatable salad oil of practically the same quality as corn and cottonseed oils, which until now have been considered to be the premium domestic edible oils. An edible grade of linseed oil, which heretofore has been considered entirely unsuitable for edible purposes, due to objectionable odor and flavor, can be produced at small extra expense. Marine oils, which at best are not particularly adapted for edible purposes, can almost completely be deodorized.

The magnesia treatment in the case of marine oils does not, however, prevent the facile polymerization or "drying" of these oils, an undesirable property in food oils. Edible oils, such as corn, cottonseed and olive oils, can be further improved in flavor and color by magnesia treatment.

The invention has many outstanding advantages. For example, it can be practiced under the mildest conditions as an adjunct of an established process for refining edible oils. The nature and conditions are such that undesirable side reactions such as oxidation, polymerization, shifting of double bonds and other chemical reactions are avoided. The process prevents the reversion of oils without changing the essential nature of the oil, thus not affecting nutritional values. (In processes involving partial hydrogenation, the chemical nature of the oil is changed with the probable formation of "unnatural" isomers and "iso" or geometric isomers of some of the unsaturated fatty acid radicals.) The magnesia process not only prevents reversion, but also removes substances which give edible oils an undesirable appearance. At the same time, the highly desirable yellow pigments which impart a clear golden color to the oil are not removed when using the quantity of magnesia required to prevent reversion.

Soybean oil, which has been rendered non-revertible by treatment with activated magnesia, has been found to develop, upon storage, a more pronounced tendency toward oxidative rancidity, as measured by increase in peroxide content, than either unrefined soybean oil or oil that has been refined by conventional methods. While the acceleration in peroxide value is not so rapid as to cause the oil to be unsuitable, a means for overcoming the difficulty was found in an unexpected manner. In testing the effects of various other adsorptive agents, in conjunction with the activated magnesia, it was noted that an oil treated with both activated carbon and magnesia became remarkably stable against the development of oxidative rancidity.

In the process for producing the oil, we prefer to treat the oil with a mixture of magnesia and carbon in one step. The quantity of magnesia required to prevent reversion is determined as previously described. The quantity of carbon may be varied from 0.1 to 5.0 per cent based on the weight of the oil. With a medium to good grade of soybean oil, the optimum effect is attained with about 0.5 per cent. The conditions of treatment are the same as those preferred for the magnesia treatment.

Example 3

To 70,900 lbs. of neutralized, washed and dried soybean oil in a large kettle equipped with an efficient stirrer, was added 370 lbs. of activated magnesium oxide, 357 lbs. of Nuchar CEEN activated carbon and 350 lbs. of filter aid (Celite 545). The temperature of the oil was maintained at 120° F. and the mixture agitated for 3 hours. The magnesia, carbon and filter aid were filtered from the oil. The oil was then deodorized with steam under high vacuum. The finished oil was sweet, bland, and not subject to reversion or oxidative rancidity.

Since certain changes in carrying out the above process, and certain modifications in the product which embody the invention may be made without

departing from its scope, it is intended that all matter contained in the above description or shown in the accompanying drawing shall be interpreted as illustrative and not in a limiting sense.

It is also to be understood that the following claims are intended to cover all of the generic and specific features of the invention herein described, and all statements of the scope of the invention which, as a matter of language, might be said to fall therebetween.

Having described our invention, what we claim as new and desire to secure by Letters Patent is:

1. The process of treating glyceride oil, which comprises mixing said oil with activated magnesium oxide prepared by heating hydrated magnesium oxide for about three hours at a temperature lying within the range of about 350° C. to about 500° C. to stabilize the oil against reversion characteristics, and thereafter separating said oil from said magnesium oxide.

2. The process of treating soybean oil, which comprises intimately mixing said oil with activated adsorbent magnesium oxide prepared by heating hydrated magnesium oxide for about three hours at a temperature lying within the range of about 350° C. to about 500° C. to remove impurities which cause reversion characteristics to develop in said oil, filtering said mixture to separate said oil from said magnesium oxide, and then deodorizing said oil.

3. The process of treating glyceride oils adsorptively to remove impurities which cause reversion characteristics to develop therein, which comprises adding to said oil approximately 0.1 to 6.0 per cent of activated adsorbent magnesium oxide prepared by heating hydrated magnesium oxide for about three hours at a temperature lying within the range of about 350° C. to about 500° C. based on the weight of the oil, and thoroughly mixing said oil and said oxide until the latter has adsorbed those impurities present in said oil which normally cause said reversion characteristics to develop.

4. The process of treating glyceride oils adsorptively to remove impurities which cause reversion characteristics to develop therein, which comprises adding to said oil approximately 0.1 to 6.0 per cent of activated adsorbent magnesium oxide prepared by heating hydrated magnesium oxide for about three hours at a temperature lying within the range of about 350° C. to about 500° C. based on the weight of the oil, and thoroughly mixing said oil and said oxide under the combined action of heat and sub-atmospheric pressure until said oxide has adsorbed those impurities present in said oil which normally cause said reversion characteristics to develop.

5. In the production of refined edible glyceride oil, the improvement which comprises subjecting said oil to treatment with an activated adsorbent magnesium oxide prepared by heating hydrated magnesium oxide for about three hours at a temperature lying within the range of about 350° C. to about 500° C. by thoroughly mixing them together, and removing from said oil, by the removal of said magnesium oxide, adsorbed impurities which cause the development of reversion characteristics in said oil.

6. The process of mixing vegetable oils with magnesium oxide prepared by heating hydrated magnesium oxide for about three hours at a temperature lying within the range of about 350° C. to about 500° C. to prevent reversion.

7. The process of contacting vegetable oils with activated magnesium oxide prepared by heating hydrated magnesium oxide for about three hours at a temperature lying within the range of about 350 C. to about 500° C. mixed with activated carbon to prevent reversion and rancidity.

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