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STABILIZATION OF OILS

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The present invention relates to the stabilization of organic products subject to oxidative deterioration, and it particularly relates to the stabilization of such products as hydrocarbon oils, paint oils, essential oils, rubber, glyceride oils, etc., by treating them with the concentrated water soluble extract of cereals and grains, and particularly when the stabilizing activity of that extract is increased in potency by heat treatment.

It has been found that certain materials such as fats may be treated by adding thereto oil soluble antioxidant materials, such as the crude vegetable oils, lecithin, etc. These materials may also be treated with the substantially oily seed materials such as crushed seasame seed, crushed peanuts, etc., wherein free oils is released following the macerating or grinding process.

The use of the substantially oily or oil soluble materials described above, in frequent cases does not give sufficient protection over a prolonged period of time. In addition, a great many products subject to deterioration are processesd at elevated temperatures such as where the hydrocarbon oils are refined at temperatures in excess of 160° C., where the glyceride oils are deodorized at temperatures in excess of 375° F., where the oils used for frying are heat treated at temperatures that at some stage exceed 250° F., where rubber, paint oils and similar materials are processed at elevated temperatures during normal refining treatments, etc. The use of heat under these circumstances is sufficient to reduce materially the antioxidant activity of such materials as the crude vegetable oils, lecithin, etc., and in many cases to inactivate them entirely.

It is among the objects of the present invention to provide improved stabilized paint, hydrocarbon, or other oils, compositions containing the same and other products subject to oxidative deterioration, the stability of which products will not be decreased by processing at elevated temperatures which might tend to destroy any antioxidant ingredients therein or oil soluble antioxidants added thereto.

Still further objects and advantages will appear from the more detailed description set forth below, it being understood, however, that this more detailed description is given by way of illustration and explanation only, and not by way of limitation, since various changes therein may be made by those skilled in the art without departing from the scope and spirit of the present invention.

In accomplishing the above objects, it has been found most satisfactory to incorporate in products subject to deterioration the water soluble extract in concentrated form of the cereals and grains such as corn, barley, oats, hominy, tapioca, rye, rice, wheat, buckwheat, etc. The preferred material for extraction contains less than 0.75% total phospholipins and less than 10% of glyceride content and it is preferably in a fine state of division. The cereal extract derived from oats and maize preferably in raw unbleached condition, dry milled and in flour or divided form gives the highest yield of stabilizing activity and is far more desirable. The cereals produce the most acceptable extract because of their low oil content which seems to enhance the production of a substantially oil-free extract as contrasted to the high oil containing materials in which the antioxidants are not as readily susceptible to water extraction.

Although the water soluble extract may be prepared in many different fashions and may be added at many stages to products subject to deterioration, it has been found most satisfactory to prepare such extract by grinding or dividing the cereal and then submerging it in or extracting it with water or an aqueous material which is to be used in the product or processing of the organic material to be stabilized.

As a general rule, the cereal undissolved portion may be removed by filtration, or the liquid may be removed by decanting, centrifuging or similar process, and the time of extraction may vary from a few seconds to a period of several hours or longer. The aqueous solvent may be employed either at room temperature or higher.

To 1 pound of cereal, there may be used, for example, 1 gallon of water or more, dependent upon the degree of concentration desired. Following a thorough mixture, the water may be removed without substantially decreasing the activity of the extract by vacuum distillation, by drying, at room temperature, or in a reducing atmosphere, etc., and the extract will take the form of a brown pasty material or a dry powdery grayish material, generally hygroscopic in character.

The extracts may not be completely soluble in the paint or hydrocarbon oil to be stabilized, but this will not decrease their efficiency as stabilizers. Where desired, the insoluble material may be filtered off preferably following heating

in the oil being stabilized to a temperature in excess of 250° F. and desirably in excess of 350° F.

This extract, in contradistinction to the crude vegetable oils, lecithin, etc., is not only unaffected by heat treatment, but is actually activated under conditions of heat. When the extract is utilized in organic products that are normally processed at high temperatures, or to which a high temperature treatment may normally be applied, minute percentages of the extract will give a marked stabilizing action.

The hydrocarbon or the paint oils, such as linseed oil, or medicinal oils, such as cod liver oil, may be treated with the concentrated water soluble extract of the cereals to markedly improve their stability, and the stabilizing effect is particularly observed when the extract is heated in the oil to temperatures in excess of 250° F. and desirably in excess of 350° F.

Example I

Linseed oil was treated with 0.1% of the concentrated water soluble extract of dry milled maize flour, said maize flour having a lecithin content of less than 0.5%. The oils were tested on the so-called Swift stability apparatus by bubbling air through samples of those oils at 208° F. until rancidity was observed as determined both organoleptically and by peroxide values, the hours given indicating the time required before rancidity could be detected.

	Hours
Control linseed oil	3
Linseed oil containing 0.2% of the extract	7
Linseed oil containing 0.2% of the extract, the entire mixture having been heated to 400° F. for 0 minutes	16

Example II

Cod liver oil was tested under similar circumstances—

	Hours
Control cod liver oil	1½
Cod liver oil plus 0.2% of the concentrated water extract of maize flour	4½
Cod liver oil plus 0.2% of the concentrated water extract of maize flour heated in the oil to 400° F. for 0 minutes	13

Although in the experiments above indicated, 0.2% of the extract was utilized, other proportions varying from 0.05% to 2% of the extract may be employed, to obtain marked stabilizing activity.

Although the concentrated water soluble extract is preferred for use with the organic materials described herein, where advisable, the unconcentrated water soluble extract of the cereals may also be employed.

Oils, such as the hydrocarbon oils, glyceride oils, essential oils, etc. are subject to rapid deterioration when in emulsified form such as the medicinal cod liver oil emulsions, petrolatum emulsions, etc. The use of the water soluble extract in the disperse water phase will materially retard such deterioration.

Example III

A regular mineral oil emulsion was prepared with 2% of water by weight to obtain a water in oil emulsion. To one lot of samples 2.0% of the water extract of oat flour was added to the water before emulsification. The samples were set aside at room temperature in the dark.

	After—		
	1 month	3 months	5 months
No treatment.	Slightly off.	Definite oxidized odor and taste.	Very bad.
Treated	O. K.	Only very slightly off in odor, taste O. K.	Little worse than 3 months, much superior to no treatment.

Surprisingly, the extract is frequently more effective than the original cereal from which the extract is obtained, even though the residue of the cereal following the extraction still retains some stabilizing properties.

Example IV

Soap was made—

A. With cocoanut oil having been previously heated to 400° F. for 0 minutes and then used in the manufacture of soap in the usual way;

B. With cocoanut oil containing the concentrated water extract of 5% of oat flour against the weight of the oil, the oil containing the extract having been heated to 400° F. for 0 minutes before manufacturing into soap;

C. With cocoanut oil containing 5% of oat flour against the weight of the oil, the oat flour having been heated in the oil to 400° F. for 0 minutes before manufacturing into soap.

The soap following manufacture was held at room temperature exposed to the air in indirect light.

	Rancidity observed after Days
Soap A	64
Soap B	130
Soap C	76

The concentrated extract obtained contains a certain amount of carbohydrate material as a result of which charring is produced when the extract is heated in the presence of the oxidizable material. Regardless of the charring, however, the extract, as indicated in the examples, becomes increasingly effective at temperatures in excess of about 250° F. and particularly at 400° F. or above so that it may readily be used in connection with materials that are normally processed at high temperatures and where other antioxidants, and particularly the oil soluble antioxidants would be inactivated or at least substantially reduced in activity.

Moreover, the extracts described, whether evaporated to dryness or not, are frequently more effective than the unextracted cereals from which they were removed, and after being in contact with the oxidizable materials for long periods, the treated materials retain their improved status for a longer period than if the original cereal were used.

Another distinct advantage in this treatment is that the presence of bulky fibrous or starchy materials is avoided when the extract is employed.

The extracts of the present invention, therefore, differ remarkably from other oil soluble antioxidant materials, such as, for example, lecithin, crude vegetable oils, etc., in that they contain a quantity of carbohydrate material, they

are not deactivated at elevated temperatures, but even become more active at temperatures as high as 400° F., for example, and they have more continued potency for longer periods of time.

Example V

Refined cottonseed oil was prepared—

A. Untreated, heated to 400° F. for 0 minutes;

B. By heating the cottonseed oil to 400° F. for 0 minutes and then adding 0.5% of the concentrated water extract of oat flour;

C. With 0.5% of the concentrated water extract of oat flour heated in the oil to 400° F. for 0 minutes.

The oils were tested on the Swift stability apparatus.

	Rancidity observed after Hours
Oil A	11
Oil B	14
Oil C	26

Example VI

20 grams of lard were prepared—

A. Untreated, heated to 400° F. for 0 minutes;

B. With 0.4 gram of oat flour heated in the oil to 400° F. for 0 minutes;

C. With 0.02 gram of the concentrated water extract of oat flour (obtained from 0.4 gram of oat flour) heated in the oil to 400° F. for 0 minutes.

The lards were tested on the Swift stability apparatus referred to above.

	Rancidity observed after Hours
Lard A	1¾
Lard B	4
Lard C	8½

It has also been observed that the relative rate of activation under conditions of heat treatment is far greater when the extract is utilized than when the proportionate amount of the unextracted cereal is utilized. For example, when maize flour is activated under conditions of heat in an oxidizable oil, its potency will be increased to only a small portion of the increase observed when the extract of that cereal used in proportionate amounts is similarly heated.

The extracts described may be applied, particularly when heat activated, not only to the paint oils, other glyceride oils, shortening, hydrogenated fats, etc., but also to the hydrocarbon oils, pharmaceutical preparations, creams, essential oils, rubber, etc. Also in the sizing of textiles and fabrics and in the manufacture of paper, board, etc., where the sizing baths comprise sulphonated oils, soaps, etc., the extracts may be employed to retard oxidation of the fabrics, their pigments, paper, etc. The extracts may be utilized either for addition to the sulphonated oils, soaps, etc., for example, and preferable heat activated, or they may be added directly to the aqueous sizing baths so that the water soluble antioxidant material penetrates the fabric or paper product.

Although the unconcentrated extract may be utilized, it is preferable for purposes of this invention to use the concentrated or dry extracts after removal of the aqueous solvent. Where water is normally used in the processing of organic materials, there may be employed either the concentrated extract or the unconcentrated extract in a dilute form.

Example VII

Where coffee is heated or roasted at a high temperature and water applied to the beans to cool and hydrate them and while the beans are at a temperature in excess of 400° F., water may be applied containing a small portion of the water soluble extract of a cereal.

Under these conditions the heat of the roasting would normally inactivate the oil soluble type of antioxidants, such as lecithin, while the cereal extracts described are on the contrary increased in potency.

There may also be employed, less desirably than the cereals, the substantially oil free seeds for purposes of extraction. For example, those oily seeds which contain in excess of 45% of oil and wherein free oil is released during any mascerating or grinding process may not be readily extracted with an oil insoluble solvent such as water. Following expression or extraction of a substantial portion of the oil, the residue may be extracted and the extract so obtained may be employed as an antioxidant in the hydrocarbon oils, other glyceride oils, paint oils, essential oils, etc., and particularly activated under conditions of heat.

The cereals and to a greater degree the de-oiled or low oil containing seeds even without extraction of the water and/or alcohol soluble portion exhibit much more marked antioxidant activity after being subjected to temperatures in excess of 250° F. and more desirably in excess of 400° F. and particularly in the presence of the oxidizable material.

However, in accordance with the present invention it is preferred to use the water extract of such materials.

Example VIII

Ground sesame seeds containing about 65% of oil were subjected to extraction with hexane. The residue following the extraction contained 0.2% of oil. Cod liver oil was prepared as follows

A. Untreated

B. Containing 0.5% of the concentrated water extract of the de-oiled sesame residue

C. Containing 0.5% of the concentrated water extract of the de-oiled sesame residue heated in the oil to 400° F.

D. Containing 1.0% of the de-oiled sesame residue

E. Containing 1.0% of the de-oiled sesame residue heated in the oil to 400° F.

The cod liver oil samples were held at 120° F. in the dark until rancidity as determined by peroxide values, was observed.

	Rancidity observed after Hours
Sample A	18
Sample B	29
Sample C	48
Sample D	22
Sample E	30

Among other less preferred materials are the substantially dry seeds capable of powdering without releasing free oil during a macerating process. For example, such seeds as cottonseed or soya may be employed particularly after the expression or extraction of the glyceride oils con-

tained therein. Care must be exercised to remove all possible water insoluble materials when preparing, for example, the water soluble extract. Any milky suspension obtained during careless or incomplete water extraction will contain water insoluble materials including glyceride oils. It is desirable to have the extract substantially free of water insoluble materials such as would be present in a milky suspension and which water insoluble materials would prove detrimental to the preparation of the extract.

Example IX

A paint oil mixture of 50% linseed oil and 50% soya bean oil was prepared as follows:

A. control

B. with 0.25% of the concentrated water extract of soya flour obtained following the expression of the soya bean oil and centrifuged to remove all water insoluble material prior to evaporating the solvent under vacuum.

C. with 0.25% of the concentrate water extract of soya flour obtained following the expression of the soya bean oil and centrifuged to remove all water insoluble material prior to evaporating the solvent under vacuum, heated in the oil to 400° F. for 0 minutes.

The oils were tested on the Swift stability apparatus above referred to

	Rancidity observed after Hours
Oil A	12
Oil B	16
Oil C	31

The extracts of the seeds differ from the extracts of the cereals in that the seed extracts are considerably higher in carbohydrate content, will char and will discolor oils particularly under conditions of heat more readily than the extracts of the cereals.

In addition to using water as the extracting medium, alcohols may be also employed, although they are less desirable. Among the alcohols that may be used are ethyl and less preferably methyl, butyl, propyl, and accepted denatured types of alcohols. In certain cases it is also possible to use polyhydric alcohols such as glycerol or other glycols, but as a general rule these polyhydric alcohols are not particularly satisfactory. The alcoholic extracts may desirably be subjected to an oil solvent extraction so as to remove such of the glycerides as happen to be present. This will not materially alter the effectiveness of the extract and particularly where the maximum water solubility is required, will be of distinct advantage. Mixtures of the alcohols and water, of course, may be employed. Oil extracting solvents, such as hexane should not be employed. The alcohol and water types of solvent are included by the expression XOH where X represents hydrogen, or a low molecular weight aliphatic group.

Although the cereals are always preferred in divided form and although in certain cases the oil bearing seeds and nuts, the oil content of which has been reduced to below 10%, may be utilized for extraction, it is possible in some cases to combine with these materials or to use alone other beans such as the cacao bean, from which a large proportion of the oily and fatty materials have been extracted or expressed, or the coffee bean in unroasted condition, both of which materials should preferably be in powdered form before extraction. Other similar materials containing water extractable carbohydrates, and, to a lesser degree, phospholipins in combination with such carbohydrates may also be employed.

By paint oils is meant particularly the substantially drying oils such as linseed, tung, soya, sunflower, poppy, etc., but the same procedures may be used for other glycerides which term includes the entire class of animal and vegetable oils and fats and compositions containing them.

By hydrocarbon oils is meant any of the homologous series such as gasoline, kerosene, hexane, petrolatum oils, etc., and also the hydrocarbon type of oils such as rubber, the terpenes, pharmaceutical creams, etc.

By essential oils is means the flavoring oils such as oil of lemon, orange, peppermint, wintergreen, the perfumes, etc.

The heat treatment for purposes of activation referred to herein should, as indicated, be desirably carried out in the presence of the oxidizable substance and should be carried out at a temperature in excess of 250° F. The higher the temperature up to about 450° F., the greater will be the increase in antioxidant activity and the proportionate increase will be far greater at temperature ranges in excess of 350° F. For example, when the heat treatment is carried out at 400° F. to 450° F., a much greater increase in antioxidant effect will be produced than where the heat treatment is only 250° F. to 300° F. For this reason it is desirable wherever practicable to subject the oxidizable material to a heat treatment of about 400° F. to 450° F. with a small amount of the stabilizing material described herein.

By the expression "seeds," is included the cereals and also the substantially de-oiled oil containing seeds and nuts, the cereals, however, being preferred and giving a more desirable and effective antioxygenic material.

The present application is a continuation in part of prior applications, Serial No. 15,307, filed April 8, 1935, and Serial No. 135,169 filed April 5, 1937.

Having thus set forth my invention, I claim:

1. A composition containing a substantially unoxidized oil, said oil being subject to oxidative deterioration upon standing or heating in the presence of air and said composition containing sufficient substantially unoxidized oil to produce deterioration of the composition upon oxidative deterioration of said oil, said oil being selected from the group consisting of the non-volatile fixed glyceride oils and fats of vegetable and animal origin, said composition containing the reaction product of a relatively small amount of an oil insoluble, carbohydrate containing fiber free and starch free antioxidant material extracted by a solvent selected from the group consisting of water and alcohol from a finely divided raw unbleached low oil and low lecithin containing cereal flour, said antioxidant material having been dispersed throughout the body of the composition, said reaction product having been formed by heating said antioxidant material with the oil at a temperature of at least about 250° F.

2. A composition containing a substantially unoxidized linseed oil, said linseed oil being subject to oxidative deterioration upon standing or heating in the presence of air and said composition containing sufficient substantially unoxidized linseed oil to produce deterioration of the composition upon oxidative deterioration of said oil, said composition containing the reaction product of a relatively small amount of an oil

insoluble, carbohydrate containing fiber free and starch free antioxidant material extracted by a solvent selected from the group consisting of water and alcohol from the cereals, said antioxidant material having been dispersed throughout the body of the composition, said reaction product having been formed by heating said antioxidant material with the oil at a temperature of at least about 250° F.

3. A substantially unoxidized linseed oil normally subject to oxidative deterioration and development of rancidity upon standing or heating in the presence of air, said oil containing the reaction product of 0.2% of the concentrated fiber and starch free carbohydrate containing water soluble extract of dry milled maize flour, said extract being dispersed throughout the body of the oil, said reaction product having been formed by heating said antioxidant material with the oil at a temperature of at least about 250° F., whereby said oil has been rendered highly resistant to oxidative deterioration.

4. A substantially unoxidized refined mineral oil emulsion normally subject to oxidative deterioration upon standing or heating in the presence of air, said emulsion containing the reaction product of about 2% of concentrated fiber and starch free carbohydrate containing water extract of oat flour, said extract being distributed throughout the body of the emulsion, said reaction product having been formed by heating said antioxidant material with the oil at a temperature of at least about 250° F., whereby said emulsion has been rendered highly resistant to oxidative deterioration.

5. The process of stabilizing composition containing substantially unoxidized oils, said oils being subject to oxidative deterioration and being present in sufficient quantity in the composition to produce deterioration of the entire composition upon oxidative deterioration of the oil therein, said oil being selected from the group consisting of the non-volatile fixed glyceride oils and fats of animal and vegetable origin, said process consisting of dispersing a small quantity of an oil insoluble, carbohydrate containing fiber free and starch free antioxidant material extracted by a solvent selected from the group consisting of water and alcohol from finely divided raw unbleached seeds in said compositions so as to assure thorough mixture with and contact between the antioxidant material and the composition and then heating to a temperature in excess of 250° F., whereby said composition and said oil contained therein are both rendered highly resistant to oxidative deterioration.

6. The process of stabilizing compositions containing substantially unoxidized oils, said oils being subject to oxidative deterioration and being present in sufficient quantity in the composition to produce deterioration of the entire composition upon oxidative deterioration of the oil therein, said oil being selected from the group consisting of the non-volatile fixed glyceride oils and fats of animal and vegetable origin, said process consisting of dispersing a small quantity of an oil insoluble, carbohydrate containing fiber free and starch free antioxidant material in said compositions so as to assure thorough mixture with and contact between the antioxidant material and the composition and then heating to a temperature in excess of 250° F., whereby said composition and said oil contained therein are both rendered highly resistant to oxidative deterioration, said antioxidant material consisting of the extract of the oil-depleted, powdery seeds obtained by the use of a solvent selected from the group consisting of water and low molecular weight aliphatic alcohols.

7. The process of stabilizing compositions containing substantially unoxidized oils, said oils being subject to oxidative deterioration and being present in suffiicent quantity in the composition to produce deterioration of the entire composition upon oxidative deterioration of the oil therein, said oil being selected from the group consisting of the non-volatile fixed glyceride oils and fats of animal and vegetable origin, said process consisting of dispersing a small quantity of an oil insoluble carbohydrate containing fiber free and starch free antioxidant material extracted by a solvent selected from the group consisting of water and alcohol from a finely divided raw unbleached cereal flour in said compositions so as to assure thorough mixture with and contact between the antioxidant material and the composition and then heating to a temperature of about 400° F. whereby said composition and said oil contained therein are both rendered highly resistant to oxidative deterioration.

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