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REFINING VEGETABLE OILS

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This invention relates, generally, to improvements in the processing or refining of vegetable oils. More particularly, the invention pertains to innovations and improvements in the washing of degummed vegetable oils, particularly soybean oil. The invention has particular utility for washing vegetable oils that have been degummed by the acid anhydride-water degumming treatment disclosed in our copending application Serial No. 333,374, filed January 26, 1953, now United States Patent No. 2,782,216, of which the present application is a continuation-in-part.

Vegetable oils, such as soybean oil, are degummed by treatment with water alone, or with water containing a minor amount of a degumming agent, so as to remove so-called "break" from the oils and either make them "break-free" or reduce their "break" content substantially. The visible dark or black flock which forms in a vegetable oil when the oil is heated is referred to in this art as "break" and a "break-free" oil is one wherein darkening and flock formation does not appear when the oil is heated. Since a particular sample of vegetable oil may contain considerable break, or may be break-free, or contain an intermediate amount of break, depending upon its origin and treatment, if any, various tests have been adopted in the industry for the purpose of rating or evaluating vegetable oils with respect to their break content. Thus, if an oil on heating to 550° F. shows no darkening or flock formation, but on the contrary tends to get lighter, i.e. "heat bleaches," such an oil is considered to be heat break-free or a non-break oil. In a more severe test, if an oil on heating to 550° F. in the presence of a specified amount of hydrochloric acid shows no darkening or flock formation but lightens in color, it is considered to be an acid break-free or Gardner break-free oil according to American Oil Chemists Society, Official Method CA 10–40, May 1949.

The so-called "break" in vegetable oils is undesirable for a number of reasons well known in the art. Accordingly, crude vegetable oil is usually subjected to a refining technique of some type so as to obtain break-free oils. The so-called "alkali refining" process has been widely used for this purpose. Essentially, this process consists of washing either crude vegetable oil or water-degummed oil with aqueous caustic solution. The by-product of this alkali refining operation is known as "soapstock" and is a dark, greasy substance consisting mainly of a mixture of soaps, neutral oil and water. The main objection to the alkali refining technique is the unavoidable loss of valuable neutral oil, partly by entrainment as neutral oil in the soapstock and partly by hydrolysis of the neutral oil. As the name implies, soapstock has very little value and is sold as a low-priced, low-grade by-product.

In addition to the alkali refining process, a number of other methods have been proposed for obtaining break-free oil. With one exception, none of these has been adopted and utilized to an appreciable extent to our knowledge. The one exception is the acid anhydride

refining technique disclosed in our above mentioned copending application, Serial No. 333,374.

In the vegetable oil refining art, the substances which separate out into the aqueous treating liquid, usually referred to as "degumming water" and which may or may not contain a "degumming agent," are commonly referred to and designated as "gum" or "gums." In the case of soybean oil, these gums after separation are dried and are marketed commercially as "lecithin." Vegetable oils that have been subjected to a treatment with water alone or to water with a small amount of degumming agent, e.g. acetic anhydride, are referred to as "degummed oils." Vegetable oil that has been treated with alkali is referred to as an "alkali refined oil" and is not usually referred to as degummed oil. As stated above, the present invention is directed to an improved technique for washing degummed oil. The benefits obtained on using the improved washing technique of the present invention are essentially three-fold:

(1) Better separation of the water and oil phases is obtained even with degummed oils while heretofore phase separation could not be achieved or could be achieved only with great difficulty.

(2) The oil losses in the washing operation are decreased since the oil content in the separated water or aqueous phase is much lower than normal.

(3) The washed degummed oils have improved color stability on heating.

In addition to these improvements there are certain other improvements and advantages obtained in practicing the present invention.

Briefly stated, the present invention involves washing a degummed vegetable oil with an aqueous solution of a dehydrated phosphatic compound of the group consisting of the water soluble polyphosphoric acids and their water soluble salts. The following commercial products are presently preferred for use in practicing this invention.

(1) Polyphosphoric acid and/or the sodium, potassium and ammonium salts thereof;
(2) Sodium hexametaphosphate;
(3) Sodium pyrophosphate;
(4) Tetraphosphoric acid; and
(5) Metaphosphoric acid.

The phosphatic washing agent used should be present in the wash water in a concentration of from 0.25 to 5% by weight of the water and the amount of water used should be from 3 to 20% based on the weight of the degummed oil being washed.

The washing operation may be carried out either batchwise as in a large kettle equipped with a stirrer, or continuously using centrifuges or other separators of known type. The washing operation may be carried out in a single washing step or in repeated washing steps. Heating and agitation improve the effectiveness of the treatment and shorten the time required. For example, in a batch washing operation, stirring of the mixture for 10 minutes at a temperature of about 175–190° F. gives very satisfactory results.

An important object of the invention is a new and improved method of washing degummed vegetable oil, particularly soybean oil, which method is capable of reducing oil losses into the aqueous phase, improving phase separation and imparting improved color stability to the oils on heating.

Another object of the invention is an improved method of washing vegetable oils which have been degummed by the use of an acid anhydride (e.g. acetic anhydride) which improved method involves washing the degummed oil with an aqueous solution of a dehydrated phosphatic washing agent.

Another important object of the invention is an improved method of refining vegetable oils, notably soybean oil, which comprises degumming the crude oil with a water solution containing a small amount of an acid anhydride (e.g. acetic anhydride), separating the degummed oil from the aqueous phase, washing the degummed oil with an aqueous solution of a dehydrated phosphatic compound, and separating the washed degummed oil from the water phase.

Certain other objects of the invention will, in part, be obvious and will, in part, appear hereinafter.

For a more complete understanding of the nature and scope of the invention, reference may now be had to the following detailed description thereof wherein illustrative examples are set forth.

This invention is broadly useful with respect to those vegetable oils which are subject to degumming. However, it has its greatest utility in connection with soybean oil which, from the commercial standpoint, is the most important vegetable oil which is degummed on a large scale. Other vegetable oils which may be degummed and washed in accordance with this invention include corn oil, cottonseed oil, peanut oil, linseed oil, perilla oil and tung oil.

Example 1

1500 grams of crude extracted soybean oil (i.e. oil obtained by the solvent extraction process) was warmed to a temperature of 140° F. and 1.5 grams of acetic anhydride was added to the oil with stirring. After 5 minutes, 22.5 grams of water was added and the mixture stirred for 15 minutes during which time the temperature was raised to 185° F. The mixture was then introduced into a batch type centrifuge and was centrifuged for 15 minutes at 1800 r.p.m. so as to separate the aqueous component containing the gums from the oil. The resulting oil was heat and acid break-free according to the Gardner-break test. The oil bleached during the Gardner test.

One 400 gram sample of the degummed oil was washed with 60 grams of tap water by stirring the water into the degummed oil and stirring the mixture for 10 minutes at 175° F. The mixture was then separated into an oil phase and a water phase by centrifuging. A second 400 gram sample of the degummed soybean oil was similarly washed with 60 grams of an aqueous solution containing 1% by weight of sodium hexametaphosphate. The washing was carried out in the same way, i.e. with stirring for 10 minutes at 175° F. The resulting mixture was then separated into an oil phase and a water phase by centrifuging.

The water phases obtained from washing the two samples of degummed oil were retained and each was evaporated to a constant weight residue. In the case of the sample that was washed with tap water alone, it was found to contain 9.9 grams or 16.5% of dry substance and this residue was soluble in hexane to the extent of 93%. The wash water from the second sample which contained the phosphate was found on evaporation to dryness to yield a residue of 4.1 grams or 6.8% dry substance. This residue was soluble in hexane to the extent of 85%.

Accordingly, the oil loss into the water phase was 2.3% oil when the degummed oil was washed with tap water alone but was only 0.88% when washed with water containing 1% sodium hexametaphosphate. Therefore, when water alone was used in the washing of the degummed oil, the loss of oil was 2½ times greater than when wash water containing the 1% sodium hexametaphosphate was used.

Example 2

Crude soybean oil was degummed with acetic anhydride as described in Example 1. Four different 400 gram samples of the degummed soybean oil were each washed with 60 ml. of the following wash solutions: (1) tap water only; (2) 0.5% water solution of metaphosphoric acid; (3) 0.5% water solution of tetraphosphoric acid; and (4) 1% water solution of sodium tetrapyrophosphate. In each instance the washing solution was stirred into the degummed oil and the mixture heated to 175° F. and stirring continued for 10 minutes. At the end of this time each mixture was separated by centrifuging into an oil phase and a water phase. The water phase from each sample was evaporated to dryness with the results shown in the following table:

Washing agent	Percent d.s. in water	Percent oil in water	Percent oil loss
(1) Water	16.4	15.1	2.2
(2) 0.5% metaphosphoric acid	4.8	4.1	0.60
(3) 0.5% tetraphosphoric acid	4.5	3.9	0.58
(4) 1% sodium tetrapyrophosphate	6.5	5.6	0.84

It will be seen that the oil loss in the sample treated with tap water only ranged from 2.6 to 3.8 times greater than for the samples that were washed with water containing one of the dehydrated phosphatic compounds.

Example 3

A sample of crude expeller corn oil was degummed by using 0.1% of acetic anhydride based on the weight of the oil and 3% water based on the weight of the oil. One 400 gram sample of the degummed corn oil was washed with 15% tap water at 175° F. with stirring for 10 minutes. A second 400 gram sample of the degummed corn oil was washed in an identical manner with 15% of a 1% aqueous solution of sodium tetraphosphate. The first sample, which was washed with water alone, gave a heavy or water phase which was in the form of a firm emulsion, not easy flowing, whereas the second sample, which was washed with a sodium tetraphosphate solution, gave a fluid free-flowing water phase. The following table gives the results of the oil losses in the two samples:

Washing agent	Percent d.s. water	Percent oil in water	Percent oil loss
(1) Water	22.7	22.3	3.5
(2) 1% solution sodium tetraphosphate	9.5	8.3	1.3

Thus, the oil loss in the sample washed with plain tap water was 2.7 times greater than the oil loss for the sample which was washed with the phosphate solution.

Example 4

Crude soybean oil was continuously degummed in a continuous oil refining plant wherein 1% acetic anhydride was first introduced into the stream of crude oil and then 2% of water was continuously introduced and the resulting mixture after being held for an average of 3 minutes in a continuous mixer was passed into a continuous centrifugal separator. Degummed oil was continuously discharged from one connection of the separator and wet gums were continuously discharged from another. The degummed oil was discharged at the rate of 5000 lbs. per hour. In one test the degummed oil was washed with plain tap water and in another test it was washed with tap water containing 1% sodium tetraphosphate. In each test the degummed oil was given two washes, the first washing being carried out at 180° F. and the second at 190° F. In each instance the plain wash water or the phosphate solution was added at the rate of 40 lbs. per hour to the degummed oil and for each of the two washes. Each of the washes lasted approximately 3 to 5 minutes and was carried out in a suitable

mixing device heated to the temperature indicated. The results of the tests are given in the following table:

	Control		1st wash sodium tetraphosphate	2nd wash (water)
	1st wash (water)	2nd wash (water)		
Percent d.s. in water	9.49	4.63	3.25	1.21
Percent oil in water	7.36	4.26	1.05	0.55
Percent oil loss (total)	0.95		0.29	

It will be seen that the oil loss in the test where plain tap water was used was approximately 3.3 times as great as for the test in which the phosphate wash solution was used.

As mentioned above, while the present invention is particularly useful in conjunction with the acetic anhydride method of refining vegetable oils, it is also useful for washing vegetable oils which have been degummed with water alone. The following example is directed to such a use:

Example 5

2500 grams of crude extracted soybean oil was heated to 140° F. and 40 grams of distilled water was added thereto with stirring. After stirring for 30 minutes the oil-water mixture was centrifuged so as to separate the hydrated gums from the oil. The degummed oil was decanted and two 400 gram samples thereof were washed, one with water alone and one with 1% sodium tetraphosphate solution. Each of the 400 gram samples of water-degummed soybean oil was heated in a water bath to 140° F. and 60 ml. of the wash water or wash solution was stirred in and stirring continued until the temperature reached 175° F., which took about 10 minutes. Each mixture was centrifuged and the water phase carefully decanted and transferred to a tared weighing dish. The total dry substance of the water phase was determined by evaporating first on a steam bath, then in a 110° C. over for 1 hour. The dry substance remaining was taken up in petroleum ether and filtered through hard paper to determine the total fat content of the water phase. The following table sets forth the results obtained:

	Control	1% sodium tetraphosphate
Percent d.s. in water phase	19.8	11.0
Percent oil in water phase	18.1	9.2
Percent oil loss	2.7	1.37

It will be seen that when water alone was used to wash soybean oil which had been degummed with water only, the oil loss was approximately twice as great as when the wash water contained 1% sodium tetraphosphate.

The following example serves to illustrate the improvement in color stability to heat achieved by washing a degummed vegetable oil with a solution of a dehydrated phosphatic compound:

Example 6

Gardner break-free oil was prepared from crude extracted soybean oil using the acetic anhydride degumming process. Two samples of the degummed soybean oil were washed, one with plain water and one with a 2% sodium hexametaphosphate solution. Color stability of the washed oil was determined by heating the oil to 600° F. and holding it at this temperature for 2 hours. After cooling, the color of the oil was compared to a standard Gardner scale and the following results were obtained:

	Gardner color after 2 hours at 600° F.
(1) No wash	Dark brown, off scale.
(2) Water wash	Do.
(3) 2.0% aqueous sodium hexametaphosphate wash	Yellow, 4-5 Gardner color.
	Yellow, 4-5 Gardner color.

It will be apparent from the foregoing description and examples tha the invention may be practiced in a number of ways and that a number of variations may be made in the foregoing examples. Obviously, instead of using a single dehydrated phosphatic compound in a washing solution, a mixture of one or more such compounds in proper proportions may be used. Alternatively, one type of phosphatic compound may be used in one washing step and another phosphatic compound used in another washing step. Furthermore, one washing step may be with plain water while another is with a solution of one of the phosphatic compounds.

Reference is made to our above mentioned copending application, Serial No. 333,374, now United States Patent No. 2,782,216, for a complete and detailed description of the acid anhydride degumming treatment in connection with which this present invention has particular utility. It is pointed out in that application that in addition to acetic anhydride, the preferred degumming agent, that other lower alkyl aliphatic monobasic and dibasic acid anhydrides may be used including propionic anhydride, butyric anhydride, maleic anhydride and succinic anhydride. The acid anhydride degumming agents should be used in an amount equal to at least about 0.05% on the basis of the weight of the oil to be degummed.

In carrying out the acid anhydrides degumming process, at least about 1.5% of water on the basis of the weight of the oil should be used and the temperature should be in the range of about 40–100° C. with sufficient agitation and holding times to effect degumming action. Several specific techniques for conducting the acid anhydride degumming process are described in copending application, Serial No. 333,374, now United States Patent No. 2,782,216.

In view of the foregoing disclosure, those skilled in the art will be able to practice the invention either according to the specific embodiments and directions set forth above, or according to other embodiments which will be obvious. Accordingly, all matter set forth above is intended to be interpreted as illustrative and not in a limiting sense.

What is claimed as new is:

1. In the processing of vegetable oils wherein a vegetable oil is degummed and the degummed oil is washed, the improvement which comprises washing the degummed vegetable oil with from 3 to 20% based on the weight of the oil of an aqueous solution containing from 0.25 to 5% based on the weight of the water of at least one water-soluble phosphatic compound each cation of which is selected from the group consisting of the hydrogen, sodium, potassium and ammonium ions and which has a negative radical selected from the group consisting of hexametaphosphate, pyrophosphate, tetraphosphate and metaphosphate.

2. In the processing of vegetable oils wherein a vegetable oil is degummed and the degummed oil washed, the improvement in washing the degummed oil which comprises mixing with the degummed oil from 3 to 20% based on the weight of the oil of an aqueous solution containing from 0.25 to 5% based on the weight of the water of at least one water-soluble phosphatic compound each cation of which is selected from the group consisting of the hydrogen, sodium, potassium and ammonium ions and which has a negative radical selected from the

group consisting of hexametaphosphate, pyrophosphate, tetraphosphate and metaphosphate, agitating the mixture at elevated temperature, and separating the oil phase and the aqueous phase.

3. The improvement called for in claim 2 wherein said mixture is heated to at least about 175° F. and intimately mixed for at least about 10 minutes.

4. In the processing of soybean oil wherein the oil is degummed and washed, the improvement which comprises washing the degummed soybean oil with from 3 to 20% based on the weight of the oil of an aqueous solution containing from 0.25 to 5% based on the weight of the water of at least one water-soluble phosphatic compound each cation of which is selected from the group consisting of the hydrogen, sodium, potassium and ammonium ions and which has a negative radical selected from the group consisting of hexametaphosphate, pyrophosphate, tetraphosphate and metaphosphate.

5. In the processing of soybean oil wherein the oil is degummed and washed, the improvement in washing the degummed soybean oil which comprises mixing with the oil from 3 to 20% based on the weight of the oil of an aqueous solution containing from 0.25 to 5% based on the weight of the water of at least one water-soluble phosphatic compound each cation of which is selected from the group consisting of the hydrogen, sodium, potassium and ammonium ions and which has a negative radical selected from the group consisting of hexametaphosphate, pyrophosphate, tetraphosphate and metaphosphate, agitating the mixture of elevated temperature, and separating the oil phase from the aqueous phase.

6. The improvement called for in claim 5 wherein said mixture is heated to at least about 175° F. and intimately mixed for at least about 10 minutes.

7. In the processing of vegetable oils wherein a vegetable oil is degummed and the degummed oil is washed, the improvement which comprises washing the degummed vegetable oil with from 3 to 20% based on the weight of the oil of an aqueous solution containing from 0.25 to 5% based on the weight of the water of sodium hexametaphosphate.

8. In the processing of vegetable oils wherein a vegetable oil is degummed and the degummed oil washed, the improvement in washing the degummed oil which comprises mixing with the degummed oil from 3 to 20% based on the weight of the oil of an aqueous solution containing from 0.25 to 5% of sodium hexametaphosphate based on the weight of the water, agitating the mixture at elevated temperature, and separating the oil phase and the aqueous phase.

9. The improvement called for in claim 8 wherein said mixture is heated to at least about 175° F. and intimately mixed for at least about 10 minutes.

10. In the processing of soybean oil wherein the oil is degummed and washed, the improvement which comprises washing the degummed soybean oil with from 3 to 20% based on the weight of the oil of an aqueous solution containing from 0.25 to 5% of sodium hexametaphosphate based on the weight of the water.

11. In the processing of soybean oil wherein the oil is degummed and washed, the improvement in washing the degummed soybean oil which comprises mixing with the oil from 3 to 20% based on the weight of the oil of an aqueous solution containing from 0.25 to 5% of sodium hexametaphosphate based on the weight of the water, agitating the mixture at elevated temperature, and separating the oil phase from the aqueous phase.

12. The improvement called for in claim 11 wherein said mixture is heated to at least about 175° F. and intimately mixed for at least about 10 minutes.

13. The method of refining a vegetable oil which comprises, treating the vegetable oil with water and a minor quantity of an acid anhydride selected from the group consisting of lower alkyl aliphatic monobasic and dibasic acid anhydrides, separating the aqueous phase from the degummed oil, and washing the degummed oil with from 3 to 20% based on the weight of the oil of an aqueous solution containing from 0.25 to 5% of at least one water-soluble phosphatic compound each cation of which is selected from the group consisting of the hydrogen, sodium, potassium and ammonium ions and which has a negative radical selected from the group consisting of hexametaphosphate, pyrophosphate, tetraphosphate and metaphosphate.

14. The method of refining soybean oil which comprises, treating soybean oil with water and a minor quantity of acetic anhydride, separating the aqueous phase from the degummed oil, and washing the degummed soybean oil with from 3 to 20% based on the weight of the oil of an aqueous solution containing from 0.25 to 5% based on the weight of the water of sodium hexametaphosphate.

15. The method of refining soybean oil which comprises, treating soybean oil with water and a minor quantity of acetic anhydride, separating the aqueous phase from the degummed oil, and washing the degummed soybean oil with from 3 to 20% based on the weight of the oil of an aqueous solution containing from 0.25 to 5% based on the weight of the water of sodium hexametaphosphate, agitating the resulting mixture heated to a temperature of at least about 175° F. for at least about 10 minutes, and separating the oil phase from the aqueous phase.

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