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OIL-PHOSPHATIDE COMPOSITION

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The present invention relates to oil-phosphatide compositions and especially to lubricating oils having reduced varnish forming properties and/or reduced emulsifying properties.

Lubricating oils used in present day automobiles and other high compression engines and the like are subject to varnish formation caused by the high temperatures and pressure to which the lubricating oil is subjected during use. Numerous treatments have been proposed to overcome this varnish formation. Phosphatides, such as may be obtained from soybeans or other sources, are useful for this purpose. Phosphatides generally available commercially are emulsifying agents. Since in normal use the lubricating agents come into contact with water the presence of these phosphatides results in stable emulsions which are undesirable.

It is accordingly an object of the invention to provide an oil-phosphatide mixture of reduced emulsifying properties.

Another object is to provide a lubricating composition of reduced or retarded emulsifying properties.

Another object is to provide a lubricating oil composition containing phosphatides which will have reduced or limited emulsifying properties.

A further object is to provide a method for decreasing varnish formation and to prevent emulsification of lubricating oils.

An additional object is to provide a method for decreasing or retarding emulsification of lubricating oils.

Further objects will appear from the description which follows.

It has been found that the desired objects of the present invention may be obtained by treating the phosphatide with an acid substance capable of reducing the pH value of the phosphatide and incorporating the thus treated phosphatide into the lubricating oil.

Compounds like phosphatides of the lecithin variety are "zwitter ions" and have long been recognized as good emulsifying agents since they contain a large oil soluble residue in the molecule as well as water soluble groupings. Thus the amino groups and the phosphoric acid groups have a tendency to be attracted to water, while the fatty acid portions would tend to be attracted to the oil. By treating the phosphatide with acid substances the charges upon the "zwitter ions" which tend to cause water solubility are neutralized with a resulting decrease in water solubility and increase in oil solubility. Since the effect of the water attracting group has been nullified or minimized the tendency to emulsification is decreased, and the oil solubility increased. Since the charges which tend to cause

water solubility are neutralized the phosphatide has its minimum solubility in water and consequently is at or near the iso-electric point.

It is important, however, that the acid substance be uniformly distributed throughout the mass. In the case of water soluble acids these may be incorporated into aqueous emulsions of the phosphatide and the emulsions then dried. This method of incorporating the acid substances is described in our copending application Serial No. 403,990, filed July 25, 1941.

Where oil soluble acids are used they are generally incorporated into a dry phosphatide-glyceride oil mixture, preferably in the molten or fluid condition.

In our copending application Serial No. 403,991, filed July 25, 1941, is described the method of incorporating oil soluble acid liberating substances such as acyl halides, sulfonyl halides, acyl pyridinium and substituted pyridinium halides. In our copending application Serial No. 403,992, filed July 25, 1941, is described the incorporation of concentrated phosphoric acid and glycerol phosphoric acid into dry phosphatide glycerol mixtures. In our copending application Serial No. 403,993, filed July 25, 1941, is described the incorporation of oil soluble sulfonic acids into phosphatide mixtures. Coacervates of phosphatides with proteins, amino acids, and similar amino compounds may also be employed. In the case of these coacervates it is believed that the charges on the phosphatide molecule are neutralized by coacervation although applicants do not wish to be bound by this theory. Weishahn Patent No. 2,198,842, dated March 26, 1940, describes the incorporation of fatty acids into the phosphatide mixture.

It has been found that when phosphatides treated according to any of the above mentioned procedures are added to lubricating oil the emulsifying tendency is reduced or substantially eliminated and at the same time the varnish inhibiting action of the phosphatide is retained.

As mentioned in the above identified applications, the addition of smaller amounts of acid or acid-liberating substances does not bring about a substantial reduction in the emulsifying properties. However, upon the addition of further amounts a sharp break in the emulsifying properties occurs, further additions beyond this point having only a slight effect upon the emulsifying property.

It is important, however, that the acid material be uniformly distributed throughout the phosphatide mass. The amount of acid material added will depend somewhat upon the particular composition of the phosphatide-oil mix-

tures and upon the particular acid used. The change in emulsifying properties appears to be dependent upon the nature of the charge or charges upon the phosphatide molecule. Thus a substantial reduction in emulsifying power does not occur the addition of the smaller quantities of acid material but appears to take place only upon the addition of a sufficient amount of acid to produce the proper reduction of the pH value of the mixture. pH values determined on the water layer formed by emulsifying lubricating oil with water and employing the acid treated phosphatide-glyceride oil mixture indicate that the pH value at which substantial reduction in emulsifying begins generally lies in the range of pH 3.7 to 4.3 or approximately 4. Applicants, however, do not wish to be understood as meaning that the pH value of the water layer is necessarily or always a true indication of the pH value of the dry mixture itself or of the true condition of the charges upon the phosphatide molecule. The pH value obtained in the water layer may depend to some extent upon the amount of the particular acid dissolved in the water. However, the dry phosphatide-oil mixture is of a lipophilic nature and consequently the pH of an aqueous solution of an acid may not necessarily represent the true condition of the charges upon the phosphatide molecule. The decrease in the emulsifying properties, however, does occur rather sharply and may be readily determined. While the emulsifying properties do not substantially decrease until this critical point is reached more acid may be added if desired and still produce the decreased emulsifying properties.

Among the acid substances which may be used may be mentioned mineral acids such as hydrochloric, sulfuric, and phosphoric; glycerol phosphoric; sulfonic acids such as benzene sulfonic acid; fatty acids such as stearic, soybean oil fatty acids, lauric, etc.; acid liberating substances such as acyl halides including stearoyl chloride and soybean oil acid chlorides, benzoyl chloride; sulfonyl halides such as toluene sulfonyl chloride; acyl pyridinium halides such as benzoyl pyridinium chlorides; and substituted pyridinium halides such as stearoyl quinolinium and stearoyl acridinium chloride.

The amount of acid or acid liberating substances used will vary somewhat depending upon the particular acid substance used but since the break in emulsifying properties is sharp the amount necessary may be readily determined. The coacervates also show inhibited emulsifying properties.

EXAMPLE I

Hydrochloric acid was added in varying amounts to aliquot parts of a soybean oil-phosphatide emulsion containing about 50% water, about 32.5% phosphatides and about 17.5% oil. The pH values of the acidified emulsions were obtained and the emulsions dried. The emulsifying properties of the mixtures of phosphatide and oil were then determined by the Navy emulsion test, United States Government Test No. 320.12, as follows:

40 ml. of water and 40 ml. of lubricating oil containing 0.1% by weight of the lubricating oil of the phosphatide-oil-acid mixture were added to a graduated cylinder. The cylinder was immersed in a heating liquid and a temperature of 180° F. was maintained during the tests. The mixtures were agitated for 5 minutes, and allowed to stand at the test temperature for specified

times. The mixtures separated into three layers, an oil layer, a water layer and an emulsion layer. The number of ml. in the emulsion layers were observed. Similar experiments were run using ammonium hydroxide to increase the pH value. The results are shown in Table I.

TABLE I

pH values	Ml. of emulsion			
	15 min.	30 min.	45 min.	60 min.
9.80.....	48.5	45.0	44.0	43.0
8.93.....	46.0	43.5	43.0	42.0
7.9.....	49.0	47.0	45.0	44.0
7.06.....	46.0	44.0	43.0	42.0
6.23.....	50.0	47.0	45.5	44.5
4.80.....	47.0	45.0	43.0	42.0
3.75.....	7.0	7.0	7.0	6.0
2.85.....	16.0	9.0	8.0	7.0
1.84.....	8.5	8.0	6.5	6.5

EXAMPLE II

To aliquot parts of a mixture of soybean phosphatides and soybean oil containing about 65 parts of phosphatide and about 35 parts of soybean oil were incorporated varying amounts of stearoyl pyridinium chloride, stearoyl chloride, toluene sulfonyl chloride, glycerol phosphoric acid and benzene sulfonic acid. The acid liberating material was incorporated by mixing at about 80° C. The emulsifying properties were determined as in Example I employing 0.1% by weight of the lubricating oil of the phosphatide-glyceride oil-acid mixture. The results are shown in Table II.

TABLE II

0.1% of phosphatide-glyceride oil-acid mix used in emulsification tests

Acid material	Amount acid used in phosphatide oil mix	Ml. of emulsion				pH of water layer
		15 min.	30 min.	45 min.	60 min.	
Untreated phosphatide.....	Per cent	49.0	46.0	46.0	44.0	6.0
Stearoyl.....	1	47.5	44.0	42.0	40.5	4.68
Pyridinium.....	2.5	43.5	40.0	39.5	38.0	4.10
Chloride.....	5.0	3.0	2.0	1.5	1.5	3.75
Do.....	10.0	3.0	3.0	3.0	3.0	3.60
Stearoyl.....	2	48.5	45.5	42.0	42.0	5.8
Chloride.....	3	35.0	26.5	16.0	13.0	5.72
Do.....	4	4.0	2.5	2.0	2.0	5.10
Do.....	5	2.5	2.0	1.5	1.0	3.42
Toluene.....	4	0.5	0.0	0.0	0.0	4.10
Sulfonyl chloride.....	5	2.0	1.0	1.0	0.5	4.05
Benzene.....	2.0	1.0	1.0	1.0	1.0	4.77
Sulfonic.....	3.5	1.5	1.0	1.0	1.0	4.37
Acid.....	6.0	2.5	2.0	2.0	2.0	4.03
Do.....	7.0	3.0	2.5	2.0	2.0	3.90
Glycerol.....	2.5	8.0	4.0	4.0	2.5	4.81
Phosphoric.....	5.0	2.5	2.5	2.0	2.0	4.31
Acid.....	20.0	8.5	5.0	4.0	3.5	3.9

EXAMPLE III

To aliquot parts of a mixture of soybean phosphatide and soybean oil containing about 65 parts of phosphatide and about 35 parts of soybean oil were incorporated 3% of soya oil fatty acid chlorides by mixing at about 80° C. When the dispersion was complete emulsification tests were then made as in Example I by employing varying amounts of this phosphatide-glyceride oil-acid chloride mixture, with the results shown in Table III.

TABLE III

3% of soya acid chlorides used with phosphatide-oil mixtures

Per cent of phosphatide-oil-acid chloride mixture used in emulsification test	Ml. of emulsion			
	15 min.	30 min.	45 min.	60 min.
Untreated phosphatide..	49.0	46.0	46.0	44.0
0.1.....	49.0	44.0	42.0	42.0
0.2.....	30.0	17.0	14.0	12.0
0.3.....	6.0	6.0	5.0	5.0

EXAMPLE IV

In this example 5% of commercial 85% concentrated phosphoric acid was incorporated with a commercially prepared soybean phosphatide-oil mixture in the same manner as described in Example I. Emulsification tests, as in Example I, were then made employing varying amounts of this phosphatide-glyceride-oil-phosphoric acid mixture, the amount of the emulsion formed and the pH of the water layer being noted. The results are shown in Table IV.

TABLE IV

5% of 85% phosphoric acid in phosphatide-oil mixture

Per cent phosphatide oil acid mixture used in emulsification	Ml. of emulsion				pH of water layer
	15 min.	30 min.	45 min.	60 min.	
Untreated phosphatide..	49.0	46.0	46.0	44.0	6.00
0.1.....	3.0	2.0	1.5	1.0	4.02
0.2.....	5.0	4.0	4.0	4.0	3.92
0.3.....	7.0	6.5	6.0	5.0	3.75

EXAMPLE V

To an emulsion of about 50% water, about 32.5% soybean phosphatides, and about 17.5% soybean oil was added a water solution containing 5% of gelatin on the basis of the weight of phosphatides contained in the emulsion. After thorough agitation, a volume of 10% hydrochloric acid solution sufficient to produce an acidity of about pH 2.0 was added. The curdy mixture was dried under vacuum in a steam-jacketed kettle equipped with a mechanical agitator. The temperature of drying was regulated at 70-80° C. The product when sufficiently dried is a fluid mass of high viscosity. To enhance the color, bleaching with benzoyl peroxide and/or hydrogen peroxide may be resorted to. The emulsifying characteristics of lubricating oil treated with three separate preparations prepared in the manner indicated were then determined by the Navy test.

TABLE V

Emulsion tests—Gelatine coacervate

Preparation	Per cent addition to oil	Ml. of emulsion			
		15 min.	30 min.	45 min.	60 min.
1.....	0.1	4	2	2	2
2.....	0.1	5	3	2.5	2
3.....	0.1	6	6	5	5
4.....	0.2	7	6	4.5	4

In addition to gelatin, other proteins and amino acids such as egg albumin or glycine may be employed.

We have given examples of the invention which have been found to be useful but they are to be considered by way of illustration and not of limitation. One skilled in the art will obviously vary the amounts of proportion of the ingredients to get optimum results.

It is not to be understood from the foregoing description that a mixture of phosphatide and glyceride oil must in all cases be treated or that the composition used necessarily in all cases contains glyceride oil. Phosphatide alone may be treated and used, or the glyceride oil may be removed from a treated phosphatide-glyceride oil mixture before use. In such cases the reduced emulsification occurs when the phosphatide has been sufficiently treated in the manner indicated.

The invention is considered to reside broadly in the use of a phosphatide which has had the charges causing emulsification sufficiently neutralized to materially reduce or prevent emulsification. Thus in addition to specially treated phosphatides those phosphatides which, due to the method of preparation from raw materials, are free from these charges may also be used.

Having described our invention, what is claimed is:

1. A difficultly emulsifiable lubricating composition suitable for lubricating high pressure internal combustion engines without substantial varnish formation, comprising a major amount of mineral lubricating oil and a minor amount of phosphatide which latter has been treated with such an amount of acid material that the charges upon the "zwitter" ions which tend to cause water solubility have been neutralized and the phosphatidic material is therefore at or near its isoelectric point.

2. A composition comprising a major amount of mineral oil and a minor amount of a phosphatide which has been treated with sufficient acid material so that the charges upon the "zwitter" ions which tend to cause water solubility have been neutralized and the phosphatide material is therefore at or near its iso-electric point.

3. The lubricating composition of claim 1 in which the phosphatide is soybean phosphatide.

4. A composition comprising a major amount of mineral oil and a minor amount of a glyceride oil containing phosphatide composition which has been treated with such an amount of acid material that the charges upon the phosphatide "zwitter" ions which tend to cause water solubility have been neutralized and the phosphatide is therefore at or near its iso-electric point.

5. The composition of claim 2 in which the acid material is oil dispersible.

6. The composition of claim 2 in which the acid material is oil dispersible and the phosphatide is soybean phosphatide.

7. The composition of claim 2 in which the phosphatide is soybean phosphatide.

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