

1

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METHOD OF PREPARING A STABLE DISPERSION OF AN INORGANIC COMPOUND IN A LUBRICATING OIL

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This invention relates to stable oil-dispersible, highly basic, metal-containing, ultra-fine compositions and methods of making the same. More particularly, this invention relates to ultra-fine dispersions of basically reactive inorganic compounds as alkaline reserve agents for use in lubricating and corrosion inhibiting compositions and is a continuation, in part, of my co-pending application, Serial No. 547,846, filed November 18, 1955, and now abandoned.

It is believed that in heavy duty detergent type lubricating oil compositions for use in diesel and like internal combustion engines, at least two requirements must be met by such oils (in addition to lubricity, stability, and the like) if a high degree of engine cleanliness is to be maintained. First, the oil must possess the power to disperse insolubles formed by fuel combustion or oil oxidation, or both, and secondly, the oil must be capable of neutralizing acidic lacquer precursors formed by either oil oxidation or interaction of the oil with sulfur acids produced from fuel combustion or both of these conditions. The detergents generally employed in oils for engine operation in high sulfur fuels (e.g., conventional metal sulfonates or phenates) are only mildly alkaline and their basicity is rapidly depleted during engine operation. Various methods have been proposed for the preparation of overbased metal sulfonates or phenates by incorporating therein various types of metal derivatives or organic compounds. While the addition of such compounds does increase the basicity of the resulting composition, the resulting composition exhibits certain disadvantages. One such disadvantage is that unless special precautions are employed, the diameter of the individual particles will be greater than desired. Small particles are desirable because the smaller the particle the greater will be the surface area available per unit weight for reaction with the acidic materials present. Also, if the diameter of the individual particles is too great, the composition will cause abrasion of the metal parts.

It is, therefore, a principal object of the present invention to provide a process which will obviate the disadvantages of the prior art processes. It is another object of my invention to provide metal-containing stable dispersions of inorganic compounds in mineral oil and process for the production of such dispersions. It is another object of my invention to provide highly useful mineral oil compositions utilizing such dispersions. Other objects of the invention will appear as the description proceeds.

To the accomplishment of the foregoing and related ends, this invention then comprises the features hereinafter fully described and particularly pointed out in the claims, the following description setting forth in detail certain illustrative embodiments of the invention, these being indicative, however, of but a few of the various ways in which the principle of the invention may be employed.

Broadly stated, the present invention comprises the process of producing a stable dispersion of an inorganic material in lubricating oil which comprises:

A. Forming an emulsion comprising—

(1) A lubricating oil,

(2) A sulfonic acid which upon neutralization produces an oil-soluble salt,

2

(3) An aqueous solution of a water-soluble inorganic basic compound,

- B. Passing an acid gas such as carbon dioxide, or sulfur dioxide, through said emulsion, thereby converting the inorganic basic compound to a substantially water-insoluble compound, the individual particles of which are less than 1 micron in diameter, and then
- C. Removing the water.

It will be obvious, of course, to those skilled in the art that the invention defined above may be practiced in a variety of ways, as, for example, the emulsion may be prepared either as an oil-in-water or a water-in-oil emulsion, depending upon the relative quantities of water and oil present. Also, as pointed out below, I generally prefer to dilute the lubricating oil with a volatile hydrocarbon and if that procedure is followed, the volatile hydrocarbon will be removed with the water in step C above.

Step C of the above described process, removing the water, could be performed by one of several alternative procedures. Thus, the water could be removed by subjecting the mixture to distillation either at atmospheric or subatmospheric pressure or the water could be removed by first mechanically separating as, for example, by decantation, siphoning, centrifugation, or drawing off a lower layer and then distillation to remove traces of water and other solvents.

Before proceeding with the specific examples illustrating my invention, it may be well to indicate in general the types of compounds required in the process.

LUBRICATING OIL

Suitable lubricating oils are mineral lubricating oils obtained by any of the conventional refining procedures and synthetic oils such as alkylene polymers as, for example, polymers of propylene, polyoxyalkylene, esters of polyoxypropylene, and dicarboxylic acid esters. Generally, it is desirable although not imperative to dilute the lubricating oil with a volatile hydrocarbon solvent, such as petroleum naphtha, or other hydrocarbons, such as hexane, heptane, octane, benzene, toluene, or xylene.

SULFONIC ACID

Suitable sulfonic acids are those which upon neutralization produce oil-soluble salts and include alkyl sulfonic acids, the so-called mahogany sulfonic acids, petroleum sulfonic acids, and the like. The industrial production of sulfonic acids from petroleum is well understood in the art and is described in the literature. Particularly useful sulfonic acids include diwaxbenzene sulfonic acid, diwaxtoluene sulfonic acid, and postdodecylbenzene sulfonic acid. The wax in making the wax aromatic sulfonic acid is obtained from different sources of crude petroleum oil. Various grades of paraffin wax are made with different melting points. A 119 to 122° F. melting point wax is a mixture of organic compounds wherein the molecular weight varies from about 330 to 340. The average carbon atom content of this mixture of organic compounds will be around 24. As the carbon atom content of the wax decreases, the melting point of the wax also decreases. Other sulfonic acids which may be used in the process of this invention include, for example, mono- and poly-wax substituted naphthalene sulfonic acid, diphenyl ether sulfonic acid, naphthalene disulfide sulfonic acid, diphenyl amine sulfonic acid, dicetyl thianthrene sulfonic acid, dilauryl betanaphthol sulfonic acid, dicapryl nitronaphthalene sulfonic acid, unsaturated paraffin wax sulfonic acid, hydroxy substituted paraffin wax sulfonic acid, tetra-amylen sulfonic acid, mono- and poly-chloro-substituted paraffin wax sulfonic acids, nitrosoparaffin wax sulfonic acids, cycloaliphatic sulfonic acids, such as laurylcyclohexyl sulfonic acids,

mono- and poly-wax substituted cyclohexyl sulfonic acids, and the like. Alternately but less preferably, I may use the corresponding sulfonate salts instead of the sulfonic acids.

A particularly useful sulfonic acid is that prepared by sulfonating postdodecylbenzene by any of the conventional methods of sulfonating alkaryl hydrocarbons such as by the treatment of a hydrocarbon with concentrated sulfuric acid, oleum, chlorosulfonic acid, etc. Postdodecylbenzene comprises monoalkylbenzenes and dialkylbenzenes in the approximate ratio of 2:3. Its typical physical properties are as follows.

Specific gravity at 38° C.....	0.8649
Average molecular weight.....	385
Percent sulfonatable.....	88
A.S.T.M., D-158 Engler:	
I.B.P. ° F.....	647
5 ° F.....	682
50 ° F.....	715
90 ° F.....	760
95 ° F.....	775
F.B.P. ° F.....	779
Refractive index at 23° C.....	1.4900
Viscosity at:	
-10° C.....centipoises.....	2800
20° C.....do.....	280
40° C.....do.....	78
80° C.....do.....	18
Aniline point.....° C.....	69
Pour point.....° F.....	-25

INORGANIC COMPOUND

Suitable inorganic basic compounds for use in my invention are restricted to those compounds which are water-soluble and which upon treatment with the acid gas are rendered substantially water insoluble. Typical inorganic basic compounds which may be used are the oxides and hydroxides of the alkali and alkaline earth metals. Specific examples of suitable basic inorganic compounds include the oxides and hydroxides of barium, lithium, and strontium. Although any of the foregoing compounds may be used, I prefer to employ either barium oxide or barium hydroxide.

As to the amount of each of the reactants, suitable and preferred quantities on a weight basis are as follows:

	Suitable (Percent)	Preferred (Percent)
Lubricating oil.....	5-25	10-20
Volatile hydrocarbon.....	0-60	20-40
Sulfonic acid.....	5-25	10-20
Inorganic compound.....	0.5-25	5-15
Water.....	10-60	10-40

The materials are admixed in any suitable reaction vessel, preferably fitted with means for agitation and heated within a temperature range of about 60 to 150° C. After mixing to form the dispersion, the acid gas is bubbled through the mixture to render the inorganic compound water-insoluble. After the reaction is completed, the temperature is gradually raised to the point at which the solvents are removed by distillation. If desired, the product may be centrifuged or filtered in order to produce a bright product but such treatment is usually unnecessary.

All of the base numbers of the products of this invention were determined by the acetic acid titration method which utilizes glacial acetic acid as the solvent and a solution of perchloric acid in glacial acetic acid as the titrant. The method is especially adapted for determinations of this type since equilibria are obtained rapidly. The procedures for carrying out acetic acid titrations are generally outlined in Analytical Chemistry, vol. 23, No. 2, February 1951, page 337, and vol. 24, No. 3, March 1952, page 519.

In order to disclose the nature of the present invention still more clearly, the following illustrative examples will be given. It is to be understood that the invention is not to be limited to the specific conditions or details set forth in these examples except insofar as such limitations are specified in the appended claims. Parts given are parts by weight. The barium hydroxide used in the examples correspond to the formula $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$.

Example 1

An aqueous solution of barium oxide was prepared by dissolving 44 parts of barium oxide in 200 parts of water. This solution was then added to 300 parts of a postdodecylbenzene sulfonic acid solution (0.56 meq./g. 24.3% acid, 24.3% white oil, and 51.4% naphtha) in a reaction vessel provided with means for heating and agitation. Heat was applied with agitation until the temperature of the contents reached 90° C. Carbon dioxide was then blown through the mixture until the mixture was acidic to alpha-naphthol benzein indicator. Upon completion of the reaction, the mixture was heated to 150° C. to remove the solvents. After removing the solvents and centrifuging, the product was bright and had a base number of 72.

Example 2

The procedure of Example 1 was repeated except 16 parts of sodium postdodecylbenzene sulfonate were added to the 300 parts of sulfonic acid prior to the addition of the aqueous barium hydroxide solution thereto. The base number of the final product was 69.

Example 3

An aqueous solution of barium hydroxide was prepared by dissolving 70 parts of barium hydroxide in 200 parts of water. This solution was then added to 300 parts of postdodecylbenzene sulfonic acid solution (0.56 meq./g. 24.3% acid, 24.3% white oil, and 51.4% naphtha) in a reaction vessel provided with means for heating and agitation. Heat was applied with agitation until the temperature of the contents reached 80° C. Carbon dioxide was then blown through the mixture until the mixture was acidic to alpha-naphthol benzein indicator. Upon completion of the reaction, the mixture was heated to 150° C. to remove the solvents. After removing the solvents and centrifuging, the product was bright and had a base number of 70.

Example 4

The procedure of Example 3 was repeated except 78 parts of sodium postdodecylbenzene sulfonate were added to the 300 parts of sulfonic acid prior to the addition of the aqueous barium hydroxide solution thereto.

Example 5

The procedure of Example 3 was followed with the exception that 80 parts of barium hydroxide was dissolved in 175 parts of water and the temperature of the contents were maintained at 80° C. for a period of 2 hours while being blown with carbon dioxide. The base number of the final product was 88 and it analyzed 19.7 percent barium.

Example 6

The procedure of Example 3 was again repeated with the exception that 90 parts of barium hydroxide was dissolved in 250 parts of water instead of 70 parts of barium hydroxide dissolved in 200 parts of water. The base number of the product was 85.

Example 7

An aqueous solution of barium hydroxide was prepared by dissolving 67 parts of barium hydroxide in 300 parts of water. This solution was then added to 300 parts of a postdodecylbenzene sulfonic acid solution (.46 meq./g., 17.3% acid, 17.3% white oil, and 65.4% benzene) in a reaction vessel provided with means for heat-

5

ing and agitation. Heat was applied with agitation and the temperature of the contents was maintained at its reflux temperature for a period of 2 hours and then the contents were blown with carbon dioxide until the mixture was acidic to alpha-naphthol benzein indicator. The mixture was then heated to 150° C. to remove the solvents. After removing the solvents and centrifuging, the product was bright, had a base number of 91 and analyzed 19.2 percent barium.

Example 8

An aqueous solution of barium hydroxide was prepared by dissolving 96 parts of barium hydroxide in 400 parts of water. This solution was then added to a solution consisting of 400 parts of a 30% active barium postdodecylbenzene sulfonate (3.9% barium, .8% sodium) and 100 parts naphtha in a reaction vessel provided with means for heating and agitation. Heat was applied with agitation until the temperature of the contents reached 80° C. Carbon dioxide was then blown through the mixture until the mixture was acidic to alpha-naphthol benzein indicator. Upon completion of the reaction the mixture was heated to 150° C. to remove the solvents. After removing the solvents and centrifuging, the product was bright and had a base number of 46.

Example 9

An aqueous solution of barium hydroxide was prepared by dissolving 78 parts of barium hydroxide in 400 parts of water. This solution was then added to 300 parts of a postdodecylbenzene sulfonic acid solution (.543 meq./g., 23.6% acid, 23.6% white oil, and 52.8% naphtha) in a reaction vessel provided with means for heating and agitation. Heat was applied with agitation and the temperature of the contents was maintained at 100° C. for a period of 2 hours, after which the contents were blown with carbon dioxide at the same temperature until the mixture was acidic to alpha-naphthol benzein indicator. The mixture was then heated to 150° C. to remove the solvents. After removing the solvents and filtering, the product was bright and had a base number of 74.

Example 10

The procedure of Example 9 was repeated with the exception that 60 parts of barium hydroxide was dissolved in 300 parts of water, the contents were maintained at a temperature of 64° C. for a period of 2 hours and was blown with carbon dioxide at a temperature of 95° C. The final product had a base number of 70.

Example 11

An aqueous solution of barium hydroxide was prepared by dissolving 60 parts of barium hydroxide in 250 parts of water. This solution was then added to 300 parts of the postdodecylbenzene sulfonic acid solution used in Example 10 in a reaction vessel provided with means for heating and agitation. Heat was applied with agitation and the temperature of the contents was maintained at 100° C. for a period of 2 hours and then the contents were blown with carbon dioxide at that temperature until the mixture was acidic to alpha-naphthol benzein indicator. After removing the solvents and filtering, the product was bright and had a base number of 66.

Example 12

The procedure of Example 11 was followed with the exception that the 60 parts of barium hydroxide were dissolved in 100 parts rather than in 250 parts of water. The final product had a base number of 66.

Example 13

An aqueous solution of barium hydroxide was prepared by dissolving 45 parts of barium hydroxide in 250 parts water. This solution was then added to 300 parts postdodecylbenzene sulfonic acid solution (0.54 meq./g., 23.6% acid, 23.6% white oil, and 52.8% naphtha)

6

in a reaction vessel provided with means for heating and agitation. Heat was applied with agitation and the contents maintained at 80° C. for two hours, then blown with sulfur dioxide for one hour. Then the contents were heated to about 110° C., an equal volume of benzene was added, and the remainder of the water removed by azeotropic distillation. The benzene solution of the product was centrifuged and the benzene was then removed by heating to 150° C. A bright product was obtained which contained 10.3% barium, 4.2% sulfur, and about 5% dispersed BaSO₃.

Example 14

An aqueous solution of barium hydroxide was prepared by dissolving 52 parts barium hydroxide in 250 parts water. This solution was then added to 300 parts postdodecylbenzene sulfonic acid (0.614 meq./g., 25.4% acid, 25.4% white oil, and 49.2% naphtha) in a reaction vessel provided with means for heating and agitation. Heat was applied with agitation and the contents maintained at 80° C., for two hours, then blown with carbon dioxide until acidic to alpha-naphthyl benzein indicator. The product was then heated to 180° C., to remove solvent and water, and then filtered. A bright fluid product was obtained which had a base number of 31.

Example 15

An aqueous solution of barium hydroxide was prepared by dissolving 53 parts of Ba(OH)₂·8H₂O in 83 parts of water. This solution was then added to 300 parts of the sulfonic acid prepared by sulfonating pentadecylbenzene bottoms (0.452 meq./g., 21.9% acid, 56.2% toluene, and 21.9% white oil) in a reaction vessel provided with means for heating and agitation. Heat was applied with agitation and the contents maintained at reflux (85° C.) for one hour, then blown with carbon dioxide until the mixture was acid to alpha-naphthol benzein indicator. The product was allowed to settle overnight at 70° C. and the aqueous layer then drawn off from the organic layer. The organic layer was then heated to 180° C. to remove traces of water and toluene and filtered. A bright fluid product was obtained which had a base number of 67.

While particular embodiments of the invention have been described, it will be understood, of course, that the invention is not limited thereto since many modifications may be made, and it is, therefore, contemplated to cover by the appended claims any such modifications as fall within the true spirit and scope of the invention.

The invention having thus been described, what is claimed and desired to be secured by Letters Patent is:

1. The process of producing metal-containing, highly basic, stable dispersions of inorganic compounds in lubricating oil compositions which comprises:

A. forming an emulsion by agitation and heat within a temperature range of 60 to 150° C., a mixture consisting of a weight basis essentially of:

- (1) 5 to 25% of a lubricating oil selected from the group consisting of mineral and synthetic oils
- (2) 5 to 25% of a sulfonic acid which upon neutralization produces an oil-soluble salt
- (3) an aqueous solution of an inorganic basic compound selected from the group consisting of barium oxide and barium hydroxides, said solution being characterized further in that the amount of water varies from 10 to 60% and the amount of said inorganic basic compound dissolved in said water varies from 0.5 to 25% of the total emulsion composition.
- (4) 20 to 40% of a volatile hydrocarbon
- B. passing carbon dioxide through said emulsion until

the same is acid to alpha-naphtholbenzein indicator, whereby said inorganic basic compound is converted to water-insoluble particles having diameters less than 1 micron,

C. removing the water and any volatile hydrocarbon. 5

2. The process of claim 1 wherein the inorganic basic compound is barium oxide.

3. The process of claim 1 wherein the inorganic basic compound is barium hydroxide.

4. The process of claim 1 wherein the sulfonic acid is 10 postdodecylbenzene sulfonic acid.

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