United States Patent Office 3,021,280 Patented Feb. 13, 1962

3,021,280

METHOD OF DISPERSING BARIUM HYDROXIDE IN A NON-VOLATILE CARRIER

Robert L. Carlyle, Lake Jackson, Tex., assignor to Continental Oil Company, Ponca City, Okla., a corporation of Oklahoma

No Drawing. Filed Dec. 17, 1956, Ser. No. 628,537
19 Claims. (Cl. 252—33)

This invention relates to a process for dispersing barium hydroxide in a non-volatile carrier whereby stable compositions are formed which possess detergency and increased reserve basicity. Such compositions find special utility as additives in lubricating oil and are likewise useful as corrosion inhibiting compositons and smilar purposes.

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 second, 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.

Many attempts have been made heretofore to produce substances which possess an alkaline reserve whereby the acidic materials formed in lubricating oils during use may be neutralized. One proposed method is that described by Bergstrom in Patents 2,270,577 and 2,279,086 utilizing basic soaps. These basic soaps demonstrated a certain superiority, and further attempts were made to increase the basicity of such soaps. One of the earliest patents referring to these basic soaps or as they were sometimes called over-based soaps or metal complexes is McNab 2,418,894. Other workers in this field include Griesinger et al., 2,402,325. These patentees suggested the use of a neutralizing agent up to about 220% of the theoretical amount required for the complete neutralization of the acid from which the soap was made. The work of Griesinger et al. was followed by Campbell and Dellinger as described in their Patent 2,485,861. These particular patentees base their disclosure on the hypothesis that minor amounts of alkaline earth metal hydroxide or carbonate can be peptized by means of an oil mahogany sulfonate. Mertes, 2,501,731, described a process whereby the normal soap is first formed and then an additional base combined therewith by a more or less simple mixing and heating operation followed by filtration. Utilizing the basic disclosure of Mertes, Asseff et al., 2,616,924, disclose a process whereby a much larger amount of metal or base may be combined with the normal soap, thus forming a complex which may be dispersed in a lubricating oil and, because of the excess metal present, possesses an alkaline reserve. The invention of Asseff et al. is an improvement over the Mertes disclosure in that Asseff et al. employed a so-called promoter. Generally these promoters are alkylated phenols.

Van Ess et al., 2,585,520, disclose a process for the preparation of a basic salt by first combining in an anhydrous state the normal salt of the acidic material and an alcoholate of the desired metal. The mass is heat-treated for a substantial length of time, filtered, and then the alcoholate is hydrolyzed to the hydroxide for the purpose of providing a basic product.

Although the products produced by the methods described above possess an alkaline reserve suitable for neutralizing acidic contaminants, there are a number of disadvantages inherent in all of these processes. As one disadvantage, the formation of the complex involves a heating process over a rather extended period of time. Another disadvantage which is even more objectionable from an operating standpoint is that the sizes of the individual particles suspended in the oil vary greatly, from extremely small particles to particles which in many cases exceed ten microns in diameter. The larger size particles are objectionable for two reasons: (1) their presence imparts a haze to the oil and (2) it is generally conceded that if the particles exceed five microns in diameter, the resulting product will have a certain abrasive action upon the metal bearings. Before use the product, therefore, must be filtered. Obviously, filtration increases the cost of operation, and the larger particles retained on the filter must be discarded.

It is therefore a principal object of the present invention to provide a process for preparing a stable dispersion of barium hydroxide in a non-volatile carrier which process obviates the disadvantages of the prior art process. It is another object of my invention to provide a highly useful mineral oil composition utilizing such dispersions. These and other objects and advantages 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 a process for preparing a stable dispersion of barium hydroxide in non-volatile carrier compositions which comprises:

A. Admixing under atmospheric conditions of temperature and pressure—
   (1) An oil soluble dispersing agent and volatile solvent therefor
   (2) A non-volatile carrier for the dispersing agent
   (3) An aliphatic alcohol solution of an oil insoluble barium inorganic base wherein the anion of said base is selected from the group consisting of oxide and hydroxide radicals
   (4) Water
B. Removing the residual solvents and water to condense from such a mass oil insoluble barium hydroxide in stably dispersed particles, the diameter of which are less than 0.25 micron

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

DISPERSING AGENTS

In general suitable dispersing agents include oil soluble sulfonic acids, metal sulfonates, ammonium sulfonates, and amine sulfonates. These dispersants may, of course, be altered chemically during the dispersion process by action of the oil insoluble barium inorganic compound. For example, if a sulfonic acid is used as dispersant, it is neutralized in the process by a portion of the barium inorganic base and becomes a barium sulfonate. Usually, the use of sulfonic acids is preferred for economic reasons rather than separate manufacture of a sulfonate prior to the dispersion process. By using a preformed sulfonate, it is possible to obtain compositions wherein the cation of the sulfonate dispersant is other than barium.

Whether sulfonic acids or preformed sulfonates are used, it is desirable to avoid appreciable amounts of sulfuric acid or salts of same in the dispersant. If these

contaminants are present, the final products tend to be slightly hazy and require centrifugation or filtration for clarification.

When sulfonic acids are used, I add from about 1½ to 7 times the quantity of the oil-insoluble inorganic compound than will react with the sulfonic acid, thus insuring the presence of an inorganic compound in the product as a dispersoid.

In most cases sulfonic acids are purified in the presence of suitable volatile solvents, hence are customarily used in this form in the process of this invention. Solvents are desirable to reduce viscosity during processing. Suitable solvents include aliphatic alcohols, aliphatic hydrocarbons, aromatic hydrocarbons, and the like. Specific examples include methanol, hexanol, capryl alcohol, benzene, toluene, hexane, various petroleum distillates such as naphthas, and mixtures of these solvents, etc.

Sulfonates which are suitable are oil soluble and include alkyl sulfonates, alkaryl sulfonates, the so-called mahogany or petroleum soaps, and the like. The mahogany soaps include particularly the oil-soluble aromatic sulfonates from petroleum. Many of the aromatic sulfonates have cycloalkyl (i.e., naphthenic) groups in the side chains attached to the benzene ring. The industrial production of oil-soluble mahogany sulfonates from petroleum is well understood in the art and is described in the literature. Normally, the alkyl sulfonates require about 24 carbon atoms for oil solubility. The alkaryl sulfonates, however, require an alkyl portion totaling only about 18 carbon atoms. To attain the requisite oil solubility, therefore, requires that the hydrocarbon portion of the sulfonate have a molecular weight between about 350 and 1,000. Preferably this molecular weight is between 400 and 700. Particularly useful sulfonates include postdodecylbenzene sulfonates, diwaxbenzene sulfonates, diwaxtoluene sulfonates, and poly nonyl naphthalene sulfonates; barium and calcium postdodecylbenzene sulfonates being preferred. A particularly useful sulfonate for use in my invention, because of its availability and commercial importance, is the sulfonate obtained by neutralizing postdodecylbenzene sulfonic acid which in turn is obtained by the sulfonation of postdodecylbenzene. Postdodecylbenzene consists of monoalkylbenzenes and dialkylbenzenes in the approximate ratio of 2:3. Its typical properties are as follows:

Specific gravity at 114° F.	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 73° F.	1.4900
Viscosity at:	
14° F. centipoises	2800
68° F.	280
104° F.	78
176° F.	18
Aniline point ° F.	156
Pour point ° F.	−25

The wax used in making the wax aromatic sulfonate is obtained from different sources of crude petroleum oil. Various grades of paraffin wax are made with different melting points. The 126–128° F. (52.2–53.3° C.) melting point wax is a mixture of organic compounds with the molecular weight averaging in the range of 330–340. The average carbon content of this mixture of organic compounds will be around 24. As the melting point of the wax decreases the carbon content of the mixture will average as low as 18 or a little lower.

Wax aromatic sulphonic acids are prepared by passing chlorine into wax at about 203° F. until the wax gains by weight about one atom of chlorine per mole of wax. The chlorowax obtained is then blown with nitrogen to remove occluded chlorine and hydrogen chloride and reacted with excess aromatic hydrocarbon in the presence of aluminium chloride at about 140° F. for about 2 hours. Monowax aromatic hydrocarbon is obtained as a residue when the aromatic hydrocarbon is distilled from the reaction mixture. When benzene or toluene is used as the aromatic hydrocarbon monowaxbenzene or monowaxtoluene are obtained respectively. Diwax aromatic hydrocarbons are obtained by reacting one molar quantity of monowax aromatic hydrocarbon with one molar quantity of chlorowax in the presence of aluminium chloride at about 185° F. Thus, from monowaxbenzene or monowaxtoluene and chlorowax there may be prepared diwaxbenzene or diwaxtoluene respectively. The wax aromatic sulphonic acids are prepared by sulphonating the wax aromatic hydrocarbons in a conventional manner with sulphuric acid, oleum, or sulphur trioxide.

Other sulfonates which may be used in the process of this invention include, for example, mono- and poly-wax substituted naphthalene sulfonates, diphenyl ether sulfonates, naphthalene disulfide sulfonates, diphenyl amine sulfonates, dicetyl thianthrene sulfonates, dilauryl beta-naphthol sulfonates, dicapryl nitro-naphthalene sulfonates, unsaturated paraffin wax sulfonates, hydroxy substituted paraffin wax sulfonates, tetra-amylene sulfonates, mono- and poly-chloro substituted paraffin wax sulfonates, nitrosoparaffin wax sulfonates; cycloaliphatic sulfonates such as laurylcyclo-hexyl sulfonates, mono- and poly-wax substituted cyclohexyl sulfonates, and the like. The expression "petroleum sulfonate" is intended to cover all sulfonates derived from petroleum products.

NON-VOLATILE CARRIER

Suitable non-volatile carriers include mineral oils, high boiling petroleum hydrocarbons, and various synthetic lubricants. Specific examples of suitable synthetics include aliphatic diesters (such as di-isooctyl azelate), silicate esters (such as hexa-2-ethyl butoxy disiloxane), and and poly alkylene glycols or their ether derivatives In cases where the product of this invention is to be used as an additive to mineral oils, the carrier will usually be a mineral oil such as a solvent refined Mid-continent lubricating oil of 100 S.S.U. @ 100° F. Similarly, if the product is to be used in synthetic oils, the vehicle will usually be a synthetic lubricant.

ALCOHOL SOLUTIONS OF INORGANIC BASE

The suitable barium containing inorganic bases are restricted to barium hydroxide, its hydrates, and barium oxide. For reasons of greater solubility in aliphatic alcohols, I prefer to use barium oxide.

Only a few aliphatic alcohols are suitable for use in the process of my invention because of limited solubility for barium oxide and barium hydroxide. These include alcohols of the aliphatic series wherein the carbon content varies from one to three. Of these alcohols, I generally prefer methanol, because it is available at a more economical price than the other alcohols; and furthermore it may be more easily removed from the final product.

WATER

The presence of at least a minor amount of water in the reacting mixture is necessary for the production of a fluid, bright, dispersion which requires no clarification. The water is required to convert the oxide to the hydroxide and to prevent gel formation. For any specific experiment the reaction is extremely sensitive to the water content of the reaction mass. When no water is present, the reaction mass gels upon removal of the solvents. When less than the optimum quantity of water is used, an insoluble gel containing some of the oil dispersible, metal containing inorganic composition separates from the reaction mass if centrifuged or filtered, thus resulting

in the partial loss of dispersing agent and basicity from the product. Utilization of an optimum quantity of water allows the preparation of a bright, fluid, stable, oil-dispersible product. On the other hand, too much water generally results in a lowering of the base number of the finished product by reducing the amount of barium hydroxide that is dispersed. To illustrate the sensitivity of a specific preparation to the water content of the reaction mass, the following table is given:

Table I[1]

Post-dodecyl benzene sulfonic acid (parts)	170 Pale oil (parts)	Benzene (parts)	Water (parts)	Methanolic BaO Soln. B.N.=125 (parts)	Appearance of Product	Base No. of Product
15	15	285	4	75	Solid gel	
15	15	285	7	75	Very viscous	176
15	15	285	10	75	Fluid, bright	204
15	15	285	15	75	Fluid, $Ba(OH)_2$ ppted.	61

[1] Parts are by weight.

Although for any one preparation the relative amount of water required for a fluid, bright product is very critical, the optimum amount of water varies considerably from one example to another. If, for example, barium hydroxide is used as the oil insoluble barium base in place of barium oxide, or if the dispersing agent is a neutral metal sulfonate rather than a sulfonic acid, less water is required. The variation in the optimum quantity of water for specific preparations is further illustrated in the attached examples. Since there is probably some relationship between the surface active agent, the water, and gel formation, the amount of water used is based upon the quantity of surface active agent, excluding the non-volatile carrier, present. To cover all the examples, in general, the optimum amount of water may vary from 2.5 to 75 percent by weight of the dispersing agent. It should again be emphasized, however, that a preparation which requires for a satisfactory product an optimum of 10 percent water, based upon the dispersing agent, would probably give unsatisfactory products if 5 percent or 15 percent water were used. Note also that in Table I 67 percent water (based on the weight of the dispersing agent) gave a satisfactory product but both 50 percent and 100 percent water gave unsatisfactory products.

In carrying out the preferred aspects of this invention, the oil-insoluble inorganic barium compound is first admixed with a polar solvent for the metal compound. This mixture is then caused to come into intimate contact with an oil-soluble surface active agent, water, and an organic solvent (second solvent) for the surface active agent. The polar solution may be added to a mixture of the other materials or the ingredients of the composition may be brought together one at a time or in any other combination except that the water should not be allowed to contact the polar solution first, since precipitation of the hydroxide may occur. Any desired amount of the oil-soluble surface active agent may be used as the starting material. Using the surface active agent as a basis, the amount of the basically reacting metal compound should be from about 1½ to 7 times that required to react with the acid when the surface active salt is formed in situ. If the surface active agent is a salt initially the amount of the inorganic compound used may be correspondingly reduced.

The organic (second) solvent for the dispersing agent should be present in an amount at least sufficient to maintain the mixture in a homogeneous mass during distillation and preferably in an amount such that some remains after the lower boiling polar solvent and water are removed. Generally suitable volume ratios of the second solvent to the combined volume of the other components may vary from about 10:1 to 5:1. Preferably, however, that ratio should vary from about 6:1 to 3:1. The actual ratio is dependent somewhat upon the size of the equipment used; there seems to be an inverse relationship between the size of the equipment and the volume of the second solvent used.

The materials are admixed at room temperature in any suitable reaction vessel, preferably fitted with means for agitation. In the course of the distillation process the mixture becomes quite viscous and unless means are provided for the agitation of the contents, that portion of the mixture adjacent to the heat exchange surfaces will be scorched. Apparently, however, rapid agitation is not necessary for the formation of a stable dispersion, as such dispersions may be produced with very slow mixing. The components of the composition are desirably combined in the presence of a hydrocarbon of synthetic oil as a diluent. After thorough admixing the temperature is gradually raised to distill off the polar solvent, water, and the second solvent. At atmospheric pressures the final temperature is usually about 300° F. Finally, the product is stripped with an inert gas such as nitrogen or methane to remove traces of solvent and water.

Alternatively, the solvents may be removed under vacuum at a maximum temperature of 150° F., thus showing that the base does not need to be "cooked" into the product. To maintain such a low temperature a pressure of from 1–20 mm. is usually required.

Under the optimum conditions the resulting product will be bright and will require no clarification. If the optimum conditions are not used, the product may be slightly hazy, and it may be desirable to centrifuge or polish filter to yield a dispersion which is crystal clear to the eye.

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 in which parts used are parts by weight. In the examples the numerical value preceding pale oil designates the S.S.U. value at 100° F.

EXAMPLE 1

With agitation 107 parts methanolic barium oxide solution having a base number of 118 was charged to a mixture consisting of 254 parts postdodecylbenzene sulfonic acid (68.0 wt. percent naphtha, 16.0 wt. percent acid, and 16.0 wt. percent pale oil), 220 parts benzene and 6 parts water. Heat was then applied to the reaction mixture to remove solvents. The temperature was raised to 302° F., then the nearly solvent free mass was further stripped at this temperature by blowing with nitrogen gas for fifteen minutes. The resulting product was a bright fluid and had a base number of 70.

EXAMPLE 2

The procedure of Example 1 was followed with the exception that the reaction mass was heated to 149° F. Then vacuum was applied, and the remaining solvents were removed by vacuum distillation at a temperature of 140–149° F. Maximum temperature was 149° F., minimum pressure was 0.06 mm. Hg, and the product was not nitrogen stripped. The resulting product was fluid and bright. The base number of the product was 69.

EXAMPLE 3

One hundred parts by volume of a solution containing 17.7 parts by weight of barium oxide in 82.3 parts by weight of methyl alcohol was admixed with 15 parts by weight of postdodecylbenzene sulfonic acid, 20 parts by weight of 170 pale oil, 356 parts by volume of benzene, and 10 parts by weight of water. The mixture was agitated and heated gradually to about 300° F. to drive off the methyl alcohol, benzene, and water. After centrifugation in benzene the product was again heated to drive off the benzene and was bright and fluid when finished. This product analyzed as follows:

Base No.		221
Barium	percent	26.87
Sulfur	do	1.95
Atomic ratio: Ba/S		3.21:1
Equivalents ratio: Ba/S		6.42:1

EXAMPLE 4

One hundred parts by volume of a solution containing 19.8 parts by weight of barium oxide in 80 parts by weight of methyl alcohol was admixed with 20 parts by weight of diwaxbenzene sulfonic acid, 55 parts by weight of 170 pale oil, 340 parts by volume of toluene, 68 parts by volume of benzene, and 10 parts by weight of water. The metal to acid hydrogen ratio of this mixture was 4.2:1. The mass was heated while being agitated until the solvents and water were removed. The product was diluted with naphtha, centrifuged, decanted, and heated further to remove the naphtha. The final product was bright and fluid and had a base number of 130.

EXAMPLE 5

A methanolic solution of barium oxide was prepared by dissolving 88 parts by weight of barium oxide in 352 parts by weight of methyl alcohol. This solution after filtration had a base number of 122. 70.5 parts by weight of a diwaxbenzene sulfonic acid (2.50 milliequivalents/gram), 202.7 parts by weight of 170 pale oil, 960.4 parts by weight of benzene, and 26.4 parts by weight of water were added to a Pfaudler reaction vessel. Two hundred parts by volume of the methanolic barium oxide solution was then slowly added while the mixture was stirred and heated to about 140° F. which caused the evaporation of the methanol-benzene azeotrope causing the precipitation of the barium oxide as a finely divided material. At this point an additional 440.5 parts by weight of benzene was added. The temperature was then gradually raised to 300° F. to remove all of the solvents, the water, and the excess benzene. The resulting product was bright, analyzed 17.4 percent barium and 1.8 percent sulfur, and had a base number of 105. The atomic ratio of barium to sulfur was 2.3:1. The ratio of equivalents, barium to sulfur, thus was 4.6:1.

EXAMPLE 6

A solution containing 22.5 parts by volume of barium oxide in a mixture made up of 40 percent methyl alcohol and 60 percent benzene was admixed with 20 parts by weight of diwaxbenzene sulfonic acid, 54 parts by weight of 170 pale oil, 285 parts by volume of benzene, and 10 parts by weight of water. The mixture was agitated constantly while the temperature was being raised to about

300° F. to drive off the solvents and water. A bright fluid product having a base number of 124 resulted.

In each of the following five examples a sulfonate was used as the acid compound starting material.

EXAMPLE 7

One hundred fifty parts by volume of a solution containing 18.5 parts by weight of barium oxide in 124.4 parts by weight of methyl alcohol was charged to a reaction vessel fitted with a mechanical agitator and containing 50 parts by weight of barium diwaxbenzene sulfonate, 144 parts by weight of 170 pale oil, 500 parts by volume of benzene, and 2 parts by weight of water. The base number of the barium diwaxbenzene sulfonate starting material was 21.1, and it contained 7.48 percent barium and 1.96 percent sulfur. The temperature of the combined mixture was raised gradually to about 300° F. to remove the solvents and water. This product was then diluted with an equal amount of benzene and centrifuged at 10,000 r.p.m. for 30 minutes separating out a small amount of sediment. The benzene solution was decanted from the precipitate and the benzene evaporated. The final product was bright and fluid and had the following analysis:

Base No.		80.5
Barium	percent	15.4
Sulfur	do	1.7
Atomic ratio: Ba/S		2.1:1
Equivalents ratio: Ba/S		4.2:1

It is seen that the basicity of the barium diwaxbenzene sulfonate product has been greatly increased by the added barium oxide as evidenced by the substantial increase in the metal content of the product and its substantially higher base number in spite of its dilution with pale oil.

EXAMPLE 8

One hundred fifty parts by volume of a solution containing 25.8 parts by weight of barium oxide in 120 parts by weight of methyl alcohol was admixed with 50 parts by weight of barium postdodecylbenzene sulfonate, 150 parts by weight of 150 raw pale oil, 700 parts by volume of 70° naphtha, and 6 parts by weight of water. The mixture was agitated and heated gradually to 300° F. to evaporate the solvents and water. This product was then diluted with naptha, centrifuged, decanted, and heated to remove the naphtha. The final product was bright and fluid and had a base number of 80.9.

EXAMPLE 9

A highly basic sulfonate containing two different alkaline earth metals was prepared by first dissolving 25.8 parts by weight of barium oxide in 120 parts by weight of methyl alcohol and adding 150 parts by volume of this solution to 50 parts by weight of calcium postdodecylbenzene sulfonate, 150 parts by weight of 150 raw pale oil, 700 parts by volume of benzene, and 15 parts by weight of water. The temperature was raised slowly while maintaining the mass under constant agitation until all of the solvents and water were removed. The product was then dissolved in naphtha, centrifuged, decanted, and heated further to remove all the naphtha. This product was bright and fluid with a base number of 63.4.

EXAMPLE 10

A highly basic product containing both an alkali metal and an alkaline earth metal was prepared by admixing 50 parts by volume of a solution containing 10 parts by weight of barium oxide in methyl alcohol with 12 parts by weight of sodium postdodecylbenzene sulfonate, 75 parts by weight of 170 pale oil, 100 parts by volume of capryl alcohol, and 2 parts by weight of water. The mass was heated under agitation until the solvents and water were removed and then was diluted with an equal amount

of naphtha and centrifuged. The naphtha solution was decanted from the small amount of barium oxide precipitated and heated to remove the naphtha. The resulting bright and fluid product had a base number of 72.3.

EXAMPLE 11

To 100 parts of barium di-nonyl naphthalene sulfonate, sold under the trade name of Na-Sul BSN by the R. T. Vanderbilt Company, was charged 220 parts of benzene. After mixing, this sulfonate solution was washed with aqueous barium chloride, aqueous methanol, and water to remove objectionable impurities. After washing the sulfonate solution was dried.

To the foregoing benzene-sulfonate solution was charged 104 parts naphtha, 70 parts benzene, 2.5 parts water, and 67 parts methanolic barium oxide (base number 118) in that order. After mixing the procedure of Example 1 was followed. The resulting product was a bright, viscous, fluid with a base number of 79.

EXAMPLE 12

The preparation of Example 1 was followed with the exception that 110 parts methanolic barium hydroxide, base number of 108, was employed instead of methanolic barium oxide. The resulting product was a bright fluid with a base number of 70.

EXAMPLE 13

One hundred parts by volume of a methyl alcohol solution saturated with barium hydroxide, $Ba(OH)_2.H_2O$, was added to a reaction vessel containing 15 parts by weight of diwaxbenzene sulfonic acid, 54 parts by weight of 170 pale process oil, 300 parts by volume of benzene, and 10 parts by weight of water. The atomic ratio of metal to acid hydrogen in the mixture was 1.62:1. The mixture was stirred constantly and the temperature gradually raised to 300° F. to remove the methyl alcohol, the benzene, and the water. The resulting product was bright and fluid and had a base number of 56.

EXAMPLE 14

With agitation 95 parts methanolic barium oxide (base number of 118) was charged to a mixture consisting of 225 parts postdodecylbenzene sulfonic acid (77.2 wt. percent naphtha, 17.8 wt. percent acid and 5.0 wt. percent unreacted postdodecylbenzene), 220 parts benzene and 3.0 parts water. Heat was then applied to the reaction mixture to remove solvents. The temperature was raised to 266° F., whereupon 28.5 parts hexa(2 ethyl butoxy) di-siloxane was added to the reaction mass. Heating was continued to a final temperature of 302° F. The nearly solvent free mass was further stripped at this temperature by blowing with nitrogen gas for fifteen minutes. The resulting product was a bright, fluid with a base number of 74.

EXAMPLE 15

The process of this invention may also be used in the preparation of dispersions of barium hydroxide with the so-called natural sulfonates, such as the mahogany sulfonates. All preceding examples were made using the so-called synthetic sulfonates or synthetic alkaryl sulfonates. In this particular example a sodium petroleum sulfonate was used which had a molecular weight of about 475. The foregoing sodium sulfonate available commercially under the trade name of "Sodium Petronate" in the amount of 1500 parts (68% active) was diluted with 491 parts of 100 pale oil to reduce the activity. The blend was heated, while stirring, under reflux temperature for 2.5 hours with 450 parts of barium chloride dissolved in 1200 parts of water. The mixture was cooled to 176° F. and 2090 parts of benzene added. It was then transferred to a separatory funnel and washed with a saturated brine solution and the layer separated. The benzene-neutral barium sulfonate layer was filtered through a bed of Hyflo yielding 4180 parts of a bright solution.

A small sample, freed of benzene by heating at 300° F. on a hot plate, analyzed as follows:

	Percent
Barium	6.7
Sodium	0.6
Sulfur	3.5

A reaction vessel was charged with 1870 parts of the above benzene solution of barium sulfonate (50% benzene), 1078 parts of benzene, 1617 parts of hexane, 30 parts of water, and 858 parts of a methanolic solution of barium oxide (base number of 120). The solvents were removed by distillation, while stirring. When the product temperature reached 257° F., the house vacuum was applied, and the temperature raised to 300° F. The final product, which weighed 932 parts, was fluid and bright. Centrifugation at 10,000 G's, R.C.F., deposited no residue. It analyzed as follows:

Base number		103
Barium	percent	18.5
Sulfur	do	2.8

As pointed out in a number of the examples (e.g., Nos. 1, 2, 11, 12, 13, 14, and 15) the crude product is obtained bright and fluid and requires no clarification. Example No. 2 points out that the dispersion may be prepared without a long heating time or cooking period as contrasted to the process of prior art. Example No. 3 illustrates the process in the preparation of a very highly basic product which contains 6.4 times the amount of barium required for the formation of a neutral product. Examples Nos. 4 through 6 illustrate the use of diwaxbenzene, and Example No. 11 illustrates the use of dinonylnaphthalene as the base hydrocarbon in contrast to the postdodecylbenzene of Examples Nos. 1 through 3. Example No. 15 illustrates the use of a natural sulfonate as a dispersing agent. To illustrate that the process may be applied to neutral metal sulfonates, including the preparation of mixed metal products, Examples Nos. 7 through 10 are given. Example No. 10 also illustrates the use of a solvent other than a hydrocarbon as the "second" solvent. The application of methanolic solutions of barium hydroxide is shown in Examples Nos. 12 and 13, and the use of a synthetic non-volatile solvent for the dispersing agent is shown in Example No. 14. The use of different and combined hydrocarbon solvents is shown in a number of the examples.

Although the finished product comprising the non-volatile diluent, the surface active agent, and the inorganic compound appears to the naked eye to be a true solution, a careful examination shows that the inorganic compound exists as a dispersoid in the other components. For example, election micrographs indicate that the average diameter of the dispersed particles range from about 0.007 to somewhat less than 1 micron with the greater portion of the particles less than 0.1 micron in diameter.

The excess barium hydroxide may be water-washed from the product to a large extent, thus demonstrating that the excess metal is not combined with the surface active agent in the form of a complex. Further evidence for this may be shown by blowing the product with either carbon dioxide or sulfur dioxide which converts the hydroxide to the carbonate or the sulfide. These barium compounds are identified as the dispersed phase by infrared analysis. These date prove that the excess metal is present as oil-insoluble barium oxide or hydroxide and not as a complex.

Lubricating compositions were prepared by adding the product of Example No. 7 and similar product prepared by the same method in varying proportions to several

blends of S.A.E. 30 mineral oil containing a small amount of added sulfur as a phosphorus pentasulfide treated wax olefin. The analyses of the highly basic products were as follows:

	Percent Ba	Percent S	Base No.
7	15.4	1.7	80.5
7(a)	13.1	1.8	60.0

The lubricating compositions thus produced were subject-to Cub engine tests. This test may be described briefly as follows: Four-cylinder Cub gasoline engines (International's light tractor engine adapted to a stand test) are run for 40 hours at 2,500 r.p.m. with 11 brake horsepower output, an oil temperature of 280° F., and a jacket temperature of 200° F. After completion of the run, the engines were disassembled and the parts were inspected, and assigned demerit ratings based on their condition. The lower the total of demerit ratings, the better is the general engine condition and the oil performance. A rating below 10 is considered to be excellent and a rating between 10 and 15 is good. Corrosion is also measured by weighing the bearing shell. A loss due to corrosion of less than 0.05 gram is considered to indicate good performance from the oil. The results of the Cub engine runs are shown below in Table II.

Table II

Blend No.	A	B	C	D	E	F
Percentage Composition:						
Product of Example 7	6.25					None
Production of Example 7(a)		6.25	6.25	4.0	7.5	None
Sulfur as P_2S_5-wax olefin	0.30	0.25	0.20	0.25	0.25	0.35
Oil	91.15	92.01	92.23	94.26	90.76	96.94
Analysis of Blend:						
Percent Ba	1.1	0.82	0.82	0.52	0.98	
Base No.	4.3	3.3	3.4	2.0	4.0	
Cub Demerit Rating	10	10	13	10		18
Bearing Corrosion Loss	0.0132	0.0343	0.0440	0.0300	0.0140	0.0573

It will be seen that the lubricating oil compositions containing the products of this invention show good overall performance in the gasoline engine as compared with Blend F containing no detergent or alkaline reserve agent.

Diesel engine tests were also made on similar lubricating compositions containing the highly basic metal-containing compounds of this invention. This test is conducted in a single cylinder Witte diesel engine using a fuel containing 2 percent sulfur. The use of such a high sulfur fuel greatly accelerates the formation of piston ring and skirt deposits, hence shortening the running time required for detergent evaluation. The run is for 50 hours at 1,800 r.p.m. with about 4½ to 5 brake horsepower output, an oil temperature of about 145° F., and a jacket temperature of 175–180° F. The condition of the piston is examined upon completion of the run and assigned a rating indicating that condition. A high rating indicates poor performance and a low rating indicates good performance. A Witte piston rating below 8 is considered to be excellent. Those between 8 and about 15 are considered to be good to fair and indicate satisfactory performance while ratings above about 20 indicate unsatisfactory performance. The results of this test are given in Table III.

Table III

Blend No.	G	H	K	L	M
Percentage Composition:					
Highly basic product of Example 7	6.25				None
Highly basic product of Example 7(a)		6.25	4.0	7.5	None
Sulfur as P_2S_5-wax olefin	0.15	0.25	0.25	0.25	0.15
Oil	92.5	92.01	94.26	90.76	98.69
Analysis of Blend:					
Percent Ba	1.1	0.82	0.52	0.98	
Base No.	4.6	3.3	2.0	4.0	
Witte Demerit Rating	4	4	6	5	47

It is seen that lubricating compositions containing the highly-basic metal compositions of this invention give improved performance ratings by greatly reducing piston deposits in diesel engine operation as compared with Blend M which contains neither detergent nor reserve alkalinity agent.

Although in the specific lubricating oil blends used in the above engine tests the highly-basic product was present in amounts ranging from 4.0 to 7.5 percent by weight of the lubricating composition, it will be understood that larger or smaller amounts may be used as desired between the ranges of about 1 to 20 percent, the amount depending in part upon the base number and the particular application to which the finished composition is to be put.

The oil portion of the lubricating blends containing the highly-basic products of this invention is preferably of the so-called mineral or hydrocarbon oils; but may also consist of wholly, or contain in part, certain fatty oils including corn oil, soybean oil, lard oil, and the like. The blends may likewise contain volatilized oils or synthetic oils of lubricating viscosity. Mineral oil is meant to include oils refined from any of the various crude oils by any of the usual refining processes including distillation, solvent extraction, acid treatment, clay treatment, dewaxing, and the like.

It will be understood that in addition to the ingredients in the above recited formulations, small amounts of other materials, all of which are conventoinal in this field, may be added as necessary and desired. These include anti-foaming agents, pour-point depressants, materials to improve the oiliness of the composition, and the like.

This application is a continuation in part of my co-pending application, Serial No. 362,970, filed June 19, 1953, and now abandoned.

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. (1) The process of forming a stable, fluid dispersion of barium hydroxide in a non-volatile carrier which comprises:

A. admixing under atmospheric conditions of temperature and pressure

(1) one part by weight of an oil-soluble dispersing agent selected from the class consisting of sulfonic acids, metal sulfonates, ammonium sulfonates and amine sulfonates;

(2) a volatile hydrocarbon solvent for said oil-soluble dispersing agent, the volume of said volatile solvent being from 3 to 10 times the combined volume of the other components;

(3) about 1 to about 6.25 parts by weight of a nonvolatile carrier selected from the group consisting of petroleum mineral oil, aliphatic diesters, silicate esters, and polyalkylene glycols;

(4) an alcoholic solution of an oil-insoluble barium inorganic base wherein the alcohol is a mono-

hydric aliphatic alcohol containing from 1 to 3 carbon atoms and the anion of said base is selected from the group consisting of oxide and hydroxide radicals and characterized further in that the amount of said inorganic base varies from about 1½ to 7 times that required to react with the sulfonic acid where this material is used as dispersing agent and ½ to 6 times the number of chemical equivalents of the dispersing agent where said dispersing agent is a salt of a sulfonic acid;

(5) 0.025 to 0.75 parts by weight of water;

B. removing the residual solvents and water by evaporation to condense from such a mass, oil-insoluble barium hydroxide in particles the diameters of which are less than 0.25 micron.

2. The process of claim 1 wherein the oil soluble dispersing agent is postdodecylbenzene sulfonic acid.

3. The process of claim 1 wherein the oil soluble dispersing agent is diwaxbenzene sulfonic acid.

4. The process of claim 1 wherein the oil soluble dispersing agent is an alkaline earth metal postdodecylbenzene sulfonate.

5. The process of claim 1 wherein the oil soluble dispersing agent is an alkaline earth metal diwaxbenzene sulfonate.

6. The process of claim 1 wherein the oil soluble dispersing agent is an alkaline earth metal dinonyl naphthalene sulfonate.

7. The process of claim 1 wherein the non-volatile carrier is hexa(2-ethyl butoxy) disiloxane.

8. The process of claim 1 wherein the barium inorganic base is barium oxide.

9. The process of claim 1 wherein the barium inorganic base is barium hydroxide.

10. The process of claim 1 wherein the oil-soluble dispersing agent is a metal alkaryl sulfonate.

11. The process of claim 1 wherein the dispersing agent is a metal sulfonate.

12. The process of claim 11 wherein the nonvolatile carrier is a petroleum mineral oil.

13. The process of claim 12 wherein the alcohol is methanol.

14. The process of claim 13 wherein the dispersing agent is barium postdodecylbenzene sulfonate.

15. The process of claim 1 wherein the oil-soluble dispersing agent is an alkaryl sulfonic acid.

16. The process of claim 15 wherein the alkyaryl sulfonic acid has a molecular weight of between 400 and 700.

17. The process of claim 16 wherein the nonvolatile carrier is a petroleum mineral oil.

18. The process of claim 17 wherein the alcohol is methanol.

19. The process of claim 18 wherein the dispersing agent is postdodecylbenzene sulfonic acid.

References Cited in the file of this patent

UNITED STATES PATENTS

2,079,051	Sullivan et al.	May 4, 1937
2,413,311	Cohen	Dec. 31, 1946
2,485,861	Campbell et al.	Oct. 25, 1949
2,501,732	Mertes	Mar. 28, 1950
2,585,520	Van Ess et al.	Feb. 12, 1952
2,614,985	Cook	Oct. 21, 1952
2,616,924	Ass Eff et al.	Nov. 4, 1952
2,671,758	Vinograd et al.	Mar. 9, 1954
2,676,925	Lindstrom et al.	Apr. 27, 1954
2,851,417	Andres	Sept. 9, 1958