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METHOD OF DISPERSING BARIUM CARBONATE IN A NON-VOLATILE CARRIER

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This invention relates to a process for dispersing barium carbonate 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 compositions and similar purposes.

It is believed that in heavy duty detergent type lubricating oil compositions for use in diesel and like internal combustion engnies, 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 carbonate 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 carbonate 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

(B.) Condensing from such mass at atmospheric pressure an oil insoluble barium carbonate in particles, the diameter of which are less than .25 micron, by passing carbon dioxide through such mass to convert the inorganic base to carbonate

(C.) Removing the residual solvents and any water present

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 4½ 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 dispersant.

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 low molecular weight alcohols, aromatic hydrocarbons, aliphatic hydrocarbons, and the like. Specific examples include methanol, benzene, hexane, and various petroleum distillates such as naphthas, 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 totalling 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 monalkylbenzenes and dialkylbenzenes in the approximate ratio of 2:3. Its typical 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.	280
40° C.	78
80° C.	18
Aniline point ° C.	69
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.

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 nitronaphthalene sulfonates, unsaturated paraffin wax sulfonates, hydroxy substituted paraffin wax sulfonates, tetra-amylene sulfonate, 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 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.

The process may be carried out using anhydrous alcohols and other reactants or in the presence of water. The fact that water can be tolerated is advantageous under certain conditions because many times commercial products cannot be obtained in an anhydrous condition; furthermore, if the surface active agent is added as an acid, a certain amount of water will be formed by the neutralization reaction.

The materials are admixed at room temperature in any suitable reaction vessel. Rapid agitation is not necessary for the formation of the stable dispersion, as such dispersions may be formed with very slow mixing. After thorough admixture, the mass is blown with carbon dioxide until conversion to carbonate is complete. This is indicated when the mass becomes acidic to alpha naphthol benzein indicator. Following carbonation the solvents and water, if any present, are normally removed by evaporation.

Alternatively, any water and the alcohol present may be removed by gravity settling after carbonation. If volatile hydrocarbon solvents are also present, they are customarily removed by evaporation. The evaporation of the solvents may be caused by the application of heat or they may be removed by the application of a vacuum, in which case it is not necessary to heat the mixture above room temperature. After the solvents have been re-

moved, the product is optically bright. Neither centrifuging nor filtering is necessary.

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

Four hundred fifty-eight parts of a solution containing 79 parts of barium oxide and 379 parts of methanol was admixed with 158 parts of postdodecylbenzene sulfonic acid, 174 parts of 170 pale oil, and 354 parts of naphtha. Carbon dioxide was passed through the mixture until all of the barium oxide was converted to barium carbonate. The mass was then agitated while the temperature was gradually raised to about 302° F. to remove the solvents and water which was formed by the neutralization of the acid. The resulting product, was bright, had a base number of 85, and analyzed 16.5 percent barium and 2.4 percent sulfur.

Example 2

Four hundred eighty-eight parts of a solution containing 84 parts of barium oxide and 404 parts of methanol was admixed with 161 parts of postdodecylbenzene sulfonic acid, 161 parts of 170 pale oil, and 339 parts of naphtha. Carbon dioxide was passed through the mixture until all of the barium oxide was converted to barium carbonate. The mass was then agitated while the temperature was gradually raised to about 302° F. to remove the solvents and water. The resulting product was bright, had a base number of 108, and analyzed 18.8 percent barium and 2.3 percent sulfur.

Example 3

Six hundred parts of a solution containing 99 parts of barium oxide and 501 parts of methanol was admixed with 161 parts of postdodecylbenzene sulfonic acid, 161 parts of 170 pale oil, and 339 parts of naphtha. Carbon dioxide was passed through the mixture until all of the barium oxide was converted to barium carbonate. The mass was then agitated while the temperature was gradually raised to about 302° F. to remove the solvents and water. The resulting product was bright, had a base number of 133, and analyzed 21.7 percent barium and 2.2 percent sulfur.

Example 4

Sixty-six parts of a solution containing 11 parts of barium oxide and 55 parts of methanol was admixed with 86 parts of barium postdodecylbenzene sulfonate, 49 parts of 170 pale oil, and 1 part of water. Carbon dioxide was passed through the mixture until all of the barium oxide was converted to barium carbonate. The mass was then agitated while the temperature was gradually raised to about 302° F. to remove the solvent and water. The resulting product was bright and had a base number of 72.2.

Example 5

Four hundred three parts of methanolic barium oxide solution having a base number of 118 was admixed with 720 parts of postdodecylbenzene sulfonic acid solution (total acidity=0.530 milliequivalent/g., oil content 20.7 wt. percent, naphtha content 58.5 wt. percent). Carbon dioxide was passed through the mixture until the mixture

was acidic to alpha naphthol benzein indicator. Maximum temperature during admixing and carbonation was 100° F. The mass was then agitated while the temperature was gradually raised to 302° F. to remove the solvents and water. The resulting product was bright, had a base number of 77, and analyzed 15.8 percent barium and 3.3 percent sulfur.

Example 6

The procedure of Example 5 was followed with the exception that after blowing the material with carbon dioxide the mixture was diluted with benzene to reduce its viscosity. The resulting solution was then filtered with a Hyflo filter aid. The benzene was removed from the filtrate by heating it to 302° F. followed by blowing with CO_2 for a period of fifteen minutes at this temperature. The resulting product was bright, had a base number of 72, and analyzed 15.4 percent barium and 3.3 percent sulfur.

Example 7

The procedure of Example 5 was followed with the exception that 6.0 parts of water was added to the mixture prior to blowing with carbon dioxide. After blowing with CO_2 and removing the solvents and water, the resulting product was bright, had a base number of 72, and analyzed 15.6 percent barium and 3.3 percent sulfur.

Example 8

The procedure of Example 7 was followed with the exception that, after the mixture was blown with carbon dioxide, the mixture was diluted with benzene to reduce its viscosity. The solution was then filtered with a Hyflo filter aid. The benzene was removed from the filtrate by heating the filtrate to 302° F. followed by blowing with carbon dioxide for fifteen minutes at this temperature. The product was bright, had a base number of 73, and analyzed 15.9 percent barium and 3.3 percent sulfur.

Example 9

The procedure of Example 5 was followed up to and including the step where carbon dioxide was passed through the mixture until the mixture was acidic to alpha naphthol benzein indicator. Following carbonation the solvents were removed from the mixture by the application of a high vacuum. The maximum temperature attained during the removal of the solvents was 108° F. and the minimum pressure was .15 mm. of mercury. The resulting product was bright, had a base number of 70, and analyzed 15.3 percent barium and 3.3 percent sulfur.

Example 10

The procedure of Example 9 was followed with the exception that 6.0 parts of water was added to the mixture prior to blowing with carbon dioxide. The solvents were removed under a pressure of .15 mm. of mercury, and the maximum temperature attained was 111° F. The resulting product was bright, had a base number of 69, and analyzed 15.1 percent barium and 3.3 percent sulfur.

Example 11

The procedure of Example 5 was followed with the exception that following blowing with carbon dioxide, the reaction mass was allowed to settle overnight after which the methanol layer was removed. The hydrocarbon phase was treated as in Example 5 wherein the solvents were removed by heating to 302° F. until the same was nearly solvent free. At this point the mass was further stripped at 302° F. by blowing with carbon dioxide for fifteen minutes. The resulting product was bright, had a base number of 71, and analyzed 14.8 percent barium and 3.2 percent sulfur.

Example 12

While stirring 69,050 pounds (10,580 gallons at 60°

F.) of a naphtha solution of an oil blend of postdodecylbenzene sulfonic acid (0.455 meq. per gram of titrateable acid and 22.3 percent oil) was mixed with 35,282 pounds (4,180 gallons at 60° F.) of a 17.3 percent methanolic solution of barium oxide. The barium oxide in excess of that required for neutralization of the sulfonic acid was converted into barium carbonate over a two-hour period by passing carbon dioxide through the solution via a sparger until the emulsion was acid to alpha naphthol benzein indicator. During conversion the temperature of the solution increased from 82 to 88° F. The solvents were then removed overhead by distillation over an eleven-hour period. Distillation time to remove about 90 percent of the solvents to a bottom temperature of 150° F. was seven hours. The remaining four hours were required to raise the temperature to 300° F. and remove most of the remaining 10 percent of solvents. Finally the product was stripped of traces of solvents by blowing for two additional hours at 300° F. with carbon dioxide. The resulting product was bright, had a base number of 70.4, and analyzed as follows:

46.6 percent active barium sulfonate
14.6 percent barium

It had a flash point of 395° F. and a viscosity at 210° F. of 249 S. U. S. Its weight in pounds per gallon at 60° F. was 9.07.

Example 13

A 30-gallon Pfaudler reactor was charged with 147.5 pounds of a benzene solution of postdodecylbenzene sulfonic acid-oil blend which contained 20.3 percent oil and titrated as 0.50 meq. per gram of acid. With this solution was mixed 72.7 pounds of a methanolic solution of barium oxide, having a base number of 128. The mixture was heated to boiling and while stirring and distilling a portion of the solvents, the unreacted barium oxide was converted into barium carbonate by blowing with carbon dioxide until the reaction mixture was acid to alpha-naphthol benzein indicator. The remaining solvents were removed by distilling to a pot temperature of 290° F. The final traces of solvents were stripped with carbon dioxide. Centrifugation of the almost bright product deposited only 0.25 lb. of residue and yielded 65 lbs. of a fluid, bright, concentrate of a basic barium sulfonate. The resulting product had a base number of 73 and analyzed as follows:

15.9 percent barium
3.1 percent sulfur

It had a flash point of 380° F. and a viscosity at 210° F. of 68.10 CS. and specific gravity at 80° F. of 1.1150.

Example 14

The process of this invention may be used in the preparation of dispersions of barium carbonate with the so-called natural sulfonates, such as the mahogany sulfonates. All the 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 500. The foregoing sodium sulfonate in the amount of 267 grams (60 percent active) was diluted with 133 grams of 100 pale oil to reduce the activity to 40 percent. This blend was heated at 200–210° F. with 80 grams of barium chloride dihydrate dissolved in 260 grams of water for 15 minutes. The mixture was transferred to a separatory funnel and stored at 149° F. overnight. The brine layer (220 ml.) was drawn off and the neutral barium sulfonate recovered. The neutral barium sulfonate obtained as outlined above was diluted with 400 ml. of hexane and mixed with 258 ml. of a methanolic barium oxide solution having a base number of 124. The mixture was stirred and blown with carbon dioxide without heating, for a period of 25 minutes until the mixture was acidic to alpha-naphthal benzein indicator. The solvents were distilled overhead to a pot temperature of 302° F. and the final traces of solvents removed under vacuum for 15 minutes. The hazy product was centrifuged for clarification and had a base number of 71.

Example 15

A mixture consisting of 1,000 parts of a neutral barium dinonyl-naphthalene sulfonate, available commercially under the trade name "Na Sul-BSN" (50 percent active barium sulfonate in mineral oil), 950 parts of naphtha and 640 parts of a methanolic solution of barium oxide (base number of 116) was stirred in a reaction vessel and blown at ambient temperature with carbon dioxide for 50 minutes. At the end of this time the barium oxide had all been converted to barium carbonate as indicated by the acid reaction of the mixture to alpha-naphthol benzein indicator. The solvents were distilled overhead and the temperature of the product raised to 302° F. Last traces of the solvents were removed by carbon dioxide stripping at 302° F. for 30 minutes. The resulting product was bright, fluid, had a base number of 68, and was obtained in a yield of 900 parts.

Example 16

A mixture consisting of 152 parts of neutral calcium postdodecylbenzene sulfonate (53 percent active in mineral oil), 133 parts of naphtha, and 100 parts of a methanolic solution of barium oxide having a base number of 118 was stirred in a reaction vessel and blown with carbon dioxide until acidic to naphthol benzein indicator. Following carbonation heat was applied to remove the solvents. The temperature was raised to 302° F. and the remaining solvents removed by blowing at that temperature with carbon dioxide for fifteen minutes. The resulting product was diluted with benzene to reduce its viscosity and filtered with a Hyflo filter aid. The benzene was removed by heating the filtrate to 302° F. followed by blowing with carbon dioxide for fifteen minutes at that temperature. The resulting product was bright and had a base number of 73.

Example 17

A mixture consisting of 150 parts of ethylene diamine dinonyl naphthalene sulfonate (50 percent active in mineral oil) available under the trade name of "Na Sul-EDS," 150 parts of naphtha, and 140 parts of a methanolic barium oxide solution having a base number of 118 was stirred in a reaction vessel and blown with carbon dioxide until acidic to alpha naphthol benzein indicator. The carbonated product was then treated as in Example 16. The final product was bright and had a base number of 84.

Example 18

A mixture consisting of 253 parts of an ethanolic barium oxide solution having a base number of 70, 200 parts of postdodecyclbenzene sulfonic acid (.64 meq./g. total acid, 27.1 parts oil and 45.8 parts naphtha) was blown with carbon dioxide until acidic to alpha naphthol benzein indicator. Maximum temperature during admixing and carbonation was 100° F. Following carbonation, heat was applied 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 carbon dioxide for fifteen minutes. The resulting product was bright and had a base number of 89.

Example 19

A mixture consisting of 200 parts of a methanolic solution of postdodecylbenzene sulfonic acid (1.11 meq./g. total acid, 44.5 parts methanol, 44.4 parts postdodecylbenzene sulfonic acid and 11.1 parts unreacted postdodecylbenzene), 71 parts 100 S. S. U. pale oil, and 239 parts methanolic barium oxide solution, having a base number of 118.6 was treated the same as in Example 18

with the exception that, after final stripping at 302° F., the product was filtered hot through Hyflo filter aid. The resulting product was bright and had a base number of 68.

Example 20

The procedure of Example 18 was followed with the exception that 185 parts of methanolic barium hydroxide solution having a base number of 92 was employed instead of ethanolic barium oxide solution. The resulting product was bright and had a base number of 84.

Example 21

A mixture consisting of 312 parts of postdodecylbenzene sulfonic acid, 75 parts of naphtha and 191 parts of methanolic barium oxide solution (base number of 118) was blown with carbon dioxide until acidic to alpha naphthol benzein indicator. After carbonation 57 parts of di-iso-octyl azelate was added to the reaction mass. The procedure of Example 18 was followed in removing the solvents and filtering. The resulting product was bright and had a base number of 70.

Example 22

The procedure of Example 21 was repeated with the exception that 57 parts of hexa(2-ethyl butoxy)disiloxane was employed instead of di-iso-azelate. The resulting product was bright and had a base number of 69.

Although the finished product comprising the oil, 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 less than 1 micron with the greater portion of the particles less than 0.03 micron in diameter.

The products of Examples 5 to 11, inclusive, were subjected to infrared examination. This examination showed the presence of an alkaline earth metal sulfonate and an alkaline earth metal carbonate. Obviously, since the only alkaline earth metal employed in the preparation of these products was barium, the presence of barium carbonate as a dispersoid in the composition is indicated.

Lubricating compositions were prepared utilizing the product prepared in accordance with the various examples listed herein. Since the results using the various compounds are very similar, a lubricating oil composition using the product of Example 12 will be given for illustrative purposes. In preparing the compounded lubricating oil, suitable and preferred ranges of the different components vary as follows: the product of Example 12, 1 to 20 percent, 2 to 6 percent; the calcium-barium phenolate sulfide, 0.25 to 3 percent, 0.75 to 2 percent; metal dithiophosphate, 0.3 to 3 percent, 0.75 to 2 percent; methyl dichlorostearate, 0.1 to 1 percent, 0.25 to 0.75 percent, respectively; and sufficient lubricating oil to make 100 percent. The calcium-barium phenolate sulfide, the metal dithiophosphate, and the methyl dichlorostearate are well-known commercially available materials which have been found to be compatible with my barium carbonate dispersions. The calcium-barium phenolate sulfide serves as an oxygen inhibitor, the metal dithiophosphate serves as a metal deactivator to reduce corrosion and to minimize metal-catalyzed oxidation of the lubricating composition. The methyl dichlorostearate enhances the oiliness and film strength of the lubricant.

The oil base with which the foregoing additives are blended is preferably of a high viscosity index and highly refined mineral lubricating oils blended to the various S. A. E. viscosity number requirements. For example, the oil blends which have been used in producing the improved lubricating compositions of this invention may be prepared from Mid-Continent solvent refined and distillation oil fractions to provide a viscosity index of about 98 and a sulfur content not exceeding about 0.1 percent.

The character of the base oil is such that with the added components above described, the finished composition should have a base number of at least about 2.0 and preferably not less than about 3.0, thus providing an engine lubricant with an actively available alkaline reserve for neutralizing service developed corrosively acidic oxidation products.

These lubricating compositions may also have added thereto, as is commonly done, an antifoaming agent, a pour point depressant, a viscosity index improver, all of which have been found generally compatible in the foregoing described lubricating compositions.

An oil composition of SAE 30 viscosity prepared in accordance with this invention contained the following:

Additives:

4.0 parts of the dispersed-$BaCO_3$ sulfonate detergent of Example 12
1.0 part Ca-Ba phenolate sulfide
1.4 parts Zn di (alkyl phenyl) dithiophosphate
0.40 part Methyl dichlorostearate

Mineral oil base:

31.8 parts neutral 170 pale oil
29.6 parts neutral 400 pale oil
31.8 parts bright stock

The foregoing lubricating composition and the base oil blend without additives were run in a Chevrolet L-4 test under the following engine conditions:

Speed	R. P. M.	3150
Load	H. P.	30
Oil sump temp	°F.	280
Water jacket temp	°F.	200

At the end of 16 hours the base oil alone showed a weight loss per half bearing (Cu-Pb alloy) of 450 milligrams. At the end of the same running time of 16 hours the base oil-additive composition of my invention gave a weight loss of about 12 milligrams.

The S. A. E. 30 lubricating composition was subjected to a Chevrolet engine valve sticking test in comparison with two competitive additive oils. The engine conditions are as follows:

Speed	R. P. M.	1500
Load	H. P.	25
Oil sump temp	°F.	120
Water jacket temp	°F.	95
Cyclic operation:		
Running	hours	3
Stopped	do	3

Valve sticking did not occur, when using the lubricating composition containing my additive until an accumulated cyclic running time of about 78 hours had been reached. Of the two competitive oils the better one did not exceed 28 hours running time until valve sticking took place.

Cam lobe and lifter wear in the presence of SAE 30 lubricating composition compiled as above containing my additive along with two competitive additive oils were determined in a General Motors cam lobe and lifter wear test (ref. G. M. LS) operating under the following engine conditions:

Speed	R. P. M.	3150
Load	H. P.	30
Oil sump temp	° F.	255
Water jacket temp	° F.	200
Valve springs overload	percent	50
Running time	hours	25

In this test the engine utilizing my new additive showed a cam lobe wear of 0.0005 inch. The nearest competitive oil had a cam lobe wear three times greater at 0.0015 inch.

The SAE 30 lubricating composition containing my additive was subjected to a detergency test along with

two competitive additive oils in a General Motors 2-cycle, 3-cycle, diesel engine (ref. G. M. 3–71) under the following engine operating conditions using a 1.0 percent sulfur fuel:

Speed	R. P. M.	1800
Load	H. P.	60
Oil sump temp	° F.	230
Water jacket temp	° F.	185

Visual examination of the pistons was made through the cylinder wall ports on stopping the engine periodically during the run on each oil. The results of engine cleanliness, i. e., time required to produce equal piston deposits was as follows: 173 hours for the engine using the S. A. E. 30 compounded oil with my additive and the nearest competitive approach was 150 hours.

My improved lubricating composition, column 1, exceeds the S–1 requirement, column 2, for a heavy duty detergent oil, and Military–0–2104 (ORD, August 4, 1950) specifications, column 3, which are less severe than the S–1 test. Military–0–2104 and S–1 are diesel engine tests; the former used on a fuel containing 0.35 percent sulfur and the latter on a fuel containing 1.0 percent sulfur.

The engine oil characteristics of our improved oil composition compared to S–1 and Military–0–2104 tested hereinabove are shown in Table I below.

TABLE I.—ENGINE OIL CHARACTERISTICS

	My Improved S–1	Approved S–1	Approved MIL–0–2104
Gravity, °A. P. I.	27.2	28.5	28.6
Flash Finished Oil	460	455	455
Viscosity, SAE	30	30	30
Viscosity Index	97	98	100
Pour Point, ° F.	0	0	0
Conradson Carbon	1.55	0.97	0.35
Sulfur	0.36	0.23	0.34
Phosphorus	0.04	0.08	0.05
Chlorine	0.07	Trace	Trace
Ash (sulfated)	1.36	0.89	0.30
Calcium	0.02		
Barium	0.67	0.34	0.12
Zinc	0.03	0.076	

An oil composition of SAE 5W–20 viscosity prepared in accordance with this invention contained the following:

Additives:

- 4.0 wt. percent of the dispersed-$BaCO_3$ sulfonate detergent of Example 12
- 1.0 wt. percent Ca-Ba phenolate sulfide
- 1.4 wt. percent zinc di(alkyl phenyl) dithiophosphate
- 0.4 wt. percent methyl dichlorostearate
- 5.50 wt. percent V. I. improver (Acryloit 710, mixed esters of polymethacrylate)

Mineral oil base:

- 71.82 wt. percent neutral pale oil, 80 S. S. U. at 100° F.
- 17.26 wt. percent neutral pale oil, 170 S. S. U. at 100° F.

The foregoing lubricating composition and a competitive oil were run in an International Harvester, U–1, 4-cylinder gasoline engine for determination of parts wear under the following engine conditions:

Speed	2500 R. P. M.
Load	Full at open throttle.
Oil sump temp	145° F.
Water jacket temp	100° F.
Engine time	100 hours.

Before each run, the various operating parts of the engine were carefully measured and dimensions noted recorded. After each run was completed, the engine was disassembled and the same parts again measured. The

dimensional differences thus obtained are a measure of the wear which occurred during the use of a particular crankcase oil.

In Table II below the superiority of my improved lubricating composition can be readily seen from the tabulation of dimensional-wear changes in comparison with the competitive oil.

TABLE II

[High load wear test—100 hrs.; International Harvester U–1 engine.]

Engine Part	Part Wear-Loss	
	My Improved Oil	Competitive Oil
Piston Ring:		
Wear, mg.	42	130
Gap Increase, inches	0.009	0.013
Babbitt Bearing, mg.	17	35
Valve Stem, inches	0.0001	0.0005
Rod Journal, do	0.00005	0.0002

As pointed out above neither is involved heat treatment nor filtration steps necessary in the preparation of the product of my invention as contrasted to the process of the prior art. These facts are brought out by Examples 5 through 11, inclusive. As for example, Example 6 is a duplicate of Example 5 with the exception that the product of Example 6 was filtered. The final products obtained in each example were very similar, and photographs of the products taken at a magnification of 21,000 diameters showed them to be practically identical. Examples 7 and 8 were duplicates of Examples 1 and 2 with the exception that one percent water was added to the composition prior to carbonation. Again the final products were practically identical and photographs taken at a magnification of 21,000 diameters showed them to be identical. The procedure used in Example 9 was the same as that employed in Example 5 except that the solvents were removed under vacuum which made it possible to carry out the entire procedure at a maximum temperature of 108° F. Again the product obtained was similar to the product obtained in Example 5. The procedure of Example 7 was followed in Example 10 with the exception that the solvents were removed under vacuum, thus making it possible to carry out the entire process at a maximum temperature of 111° F. The product obtained was similar to the product obtained in Example 7. These examples show three things: filtration is not necessary in the preparation of the product, a heat treatment is not necessary in the preparation of the product, and the absence or the presence of a small amount of water has no effect upon the final product.

There is a direct relationship between base number and the amount of barium present in excess over that present in the oil soluble dispersing agent alone. Tabulated below are data showing this relationship in dispersions of barium carbonate in a non-volatile carrier wherein the base number varies from 30 to 150. In all cases the ratio of neutral barium postdodecylbenzene sulfonate to non-volatile carrier was maintained equivalent to that of a 70 base numbered product.

TABLE III

B. N.	Percent Basic Barium	Percent Neutral Barium	Basic Barium (Percent of Neutral Barium)
30	3.68	6.74	55
50	6.13	6.50	95
70	8.57	6.26	137
100	12.25	5.88	208
120	14.72	5.62	262
135	16.56	5.43	305
150	18.38	5.25	350

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

From the foregoing examples it is apparent that the relative quantities of most of the different components used in the prepartion of a dispersion of barium carbonate in the vehicle are relatively unimportant. As for example a solvent is used merely to reduce the viscosity of the mixture as an aid in processing. Generally 0 to 5 parts of volatile solvent may be used per part of oil soluble dispersing agent. As to the amount of carrier employed, that may vary from ⅓ to 2 parts per part of oil soluble dispersing agent. Obviously a larger quantity of carrier may be used in which case the resultant concentrate will be less concentrated than if a lesser quantity were used. The amount of the inorganic base used is more important. As a general rule the amount of inorganic base added should be sufficient to increase the metal content of the resulting mixture 50 to 300 percent over that produced by the pressure of the metal in the oil-soluble dispersing agent alone.

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 forming a stable dispersion of barium carbonate in a mineral oil which comprises: (A) admixing under atmospheric conditions of temperature and pressure (1) 1 part of an oil soluble dispersing agent selected from the class consisting of sulfonic acids, metal sulfonates, ammonium sulfonates, and amine sulfonates, (2) 0–5 parts of volatile hydrocarbon solvent for said oil soluble dispersing agent, (3) ⅓ to 2 parts of a mineral oil, (4) an aliphatic alcoholic solution of an oil insoluble barium inorganic base wherein the aliphatic alcohol contains 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 4 times that required to react with the sulfonic acid where this material is used as dispersing agent and ½ to 3 times the number of chemical equivalents of the dispersing agent where said dispersing agent is a salt of a sulfonic acid; (B) condensing from the resulting mixture at atmospheric pressure an oil-insoluble barium carbonate in particles, the diameters of which are less than 0.25 micron, by passing carbon dioxide through said mixture to convert the excess barium inorganic base to the carbonate, and then (C) removing the residual solvents by evaporation.

2. The process of claim 1 wherein the hydrocarbon portion of the oil soluble dispersing agent has a molecular weight between 400 and 700.

3. The process of claim 1 wherein the oil soluble dispersing agent is postdodecylbenzene 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 barium postdodecylbenzene sulfonate.

6. The process of claim 1 wherein the oil soluble dispersing agent is calcium postdodecylbenzene sulfonate.

7. The process of claim 1 wherein the aliphatic alcoholic solution is a methanolic solution.

8. The process of claim 1 wherein the aliphatic alcoholic solution is an ethanolic solution.

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

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

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