

3,127,348

**OVER-BASED CALCIUM-CONTAINING
DETERGENT INHIBITORS**

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The present invention relates to improved detergent type calcium-containing additives for lubricating oil compositions and for oil concentrates containing such additives. The invention is particularly directed to improved processes for the manufacture of over-based calcium-containing detergent inhibitors. The additives may be characterized generally as colloidal dispersions of calcium salts, principally calcium carbonate, in admixture with phosphosulfurized hydrocarbons and alkylated phenols and/or alkyl phenol sulfides.

In recent years there has been an increasing demand for lubricating oils, particularly for piston type internal combustion engines, which will have high detergency and at the same time will possess satisfactory resistance to oxidation and freedom from corrosive tendencies. High detergency oxidation resistant lubricating oils serve to keep internal combustion engines free of varnish, sludge, and coke-like deposits, and thereby promote longer engine life through reduced wear.

Extensive investigation has indicated that complexes or colloidal dispersions of polyvalent metal salts, and particularly of alkaline earth metal salts, wherein a high ratio of metal to organic acid components exists, are very desirable as detergent and inhibitor additives for crankcase lubricants. It has been found difficult, however, to prepare colloidal dispersions of this nature, particularly in the case of calcium salts, that will be high in metal content and still have satisfactory stability as characterized by the absence of haze in the filtered product.

While previous workers in the art of lubricant additives have proposed the preparation of detergent inhibitors of the nature contemplated by the present invention by reacting alkaline earth metal oxides and/or hydroxides with carbon dioxide in the presence of alkyl phenols and phosphosulfurized hydrocarbons, the products have not been entirely satisfactory. In systems of this nature the phosphosulfurized hydrocarbon serves as a surfactant that maintains the colloidal dispersion. In previous work it was found that in order to increase the metal content of the system it was necessary to increase the amount of surfactant also. As the surfactant represents a considerable item in the overall cost of the additive composition, there has been an incentive to develop methods for attaining high ratios of metal to surfactant in stable compositions of this type. Stability depends largely upon the degree of fineness of the particles in the colloidal dispersion. This in turn is easily determined by the relative absence of haze in the finished product. A haze rating of more than 100 nephelos on a mixture of 5 weight percent of the additive in white oil is considered unacceptable.

In accordance with this invention, a low haze, light colored, calcium detergent additive having a high metal-to-surfactant ratio can be prepared by treating an oil solution of a phosphosulfurized hydrocarbon and an alkyl phenol or alkyl phenol sulfide with calcium oxide and/or calcium hydroxide and with carbon dioxide, in the presence of a nitrogen base, the latter being preferably ammonium hydroxide or more preferably ammonium hydroxide and ammonium sulfonate.

The invention is applicable whenever it is desired to prepare additives in which the ratio of calcium equivalents to surfactant equivalents is at least 3 to 1, and is operable for such ratios up to about 13 to 1. The surfactants

equivalent is determined on the basis that all of the phosphorus in the phosphosulfurized hydrocarbon is available as a monobasic acid.

Phosphosulfurized hydrocarbons for use in this invention can be prepared by reacting a sulfide of phosphorus, for example P_2S_5 , with a suitable hydrocarbon base stock which, of course, should be one that results in materials that are completely oil soluble after phosphosulfurization. The preferred hydrocarbon starting materials used in this invention are (1) terpenes such as alpha-pinene (2) heavy petroleum fractions, distillates or residua containing less than 5% of aromatics and having a viscosity of 210° F. of 140 to 250 SSU; and (3) polyolefins having a Staudinger molecular weight in the range of 500 to 200,000 and containing 2 to 6 carbon atoms per olefin monomer. Polybutenes that have Staudinger molecular weights in the range of 700 to 100,000 are particularly preferred.

Preferably the phosphosulfurized hydrocarbon is prepared by reacting approximately four moles of hydrocarbon base stock (e.g., a polyolefin) per mole of phosphorus pentasulfide. A slight excess of phosphorus pentasulfide over the 1 to 4 mole ratio can be used to insure complete phosphosulfurization. The phosphosulfurization reaction is conducted under anhydrous conditions at temperatures of 150° to 600° F. for a period in the range of 0.5 to 15 hours. A very slight amount of an alkyl phenol or alkyl phenol sulfide, preferably in the range of 0.001 to 1.0 percent by weight, can be added as a catalyst in the phosphosulfurization reaction. It has also proven very useful to treat or blow the phosphosulfurized product with an inert gas such as nitrogen for a period of 10 min. to 2 hours to aid in reducing hydrogen sulfide evolution and its corresponding odor. The preparation of phosphosulfurized hydrocarbons and the use of catalysts in the phosphosulfurization reaction are more fully described in U.S. Patent 2,875,188.

The alkyl phenol component of the reaction mixture is preferably one having a molecular weight in the range of from about 200 to about 700. For example, the alkylation product of phenol with diisobutylene or with tripropylene, i.e. nonyl phenol, may be used. In some cases it is possible to substitute for a portion or all of the alkyl phenol an alkyl phenol sulfide, which is the thioether of an alkyl phenol, i.e. a compound in which the alkylated phenol groups are joined by a divalent sulfur atom. The alkyl phenols are conveniently converted to alkyl phenol sulfides by reaction with sulfur dichloride.

The ammonium sulfonates used in practicing the present invention are the ammonium salts of sulfonic acids obtained by the sulfonation of either natural or synthetic hydrocarbons. The preferred sulfonic acids have molecular weights in the range of 300 to 700 (as the sodium soap). The synthetic sulfonic acids preferably have molecular weights in the narrower range of 400 to 600. The acids can contain more than one sulfonyl group in the molecule. Suitable sulfonic acids are produced by sulfonating alkyl aromatic hydrocarbons such as didodecyl benzene. They can also be obtained by treatment of lubricating oil base stocks with concentrated or fuming sulfuric acid in a conventional manner to produce oil-soluble "mahogany" acids.

The procedure followed in preparing the detergent inhibitor additives of this invention may be generally described as follows. A solution or blend of a phosphosulfurized hydrocarbon, an alkyl phenol, and ammonium sulfonate (where the latter is used) is prepared in a hydrocarbon oil. The hydrocarbon oil may comprise any fraction that has a sufficiently high boiling point so that it will not vaporize under the reaction conditions. Light lubricating oil fractions are particularly suitable. Ammonium hydroxide is then added to the blend, followed by water and then calcium oxide and/or calcium hydrox-

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ide. Finally, over a period of 2 or 3 hours, carbon dioxide is passed into the mixture. The reaction product is thereafter dehydrated and filtered. The broad and preferred temperature ranges and treating times for each of these steps are given in Table I.

TABLE I

Process Step	Temperature Range, ° F.	
	Broad	Preferred
1. Blend phosphosulfurized hydrocarbon, alkyl phenol, ammonium sulfonate (when used) and diluent oil.....	60-180	90-100
2. Add NH ₄ OH and stir (e.g. 10 minutes, time is not critical).....	60-180	100-130
3. Add water.....	60-180	130
4. Add dry Ca(OH) ₂ and soak (e.g. 20 minutes, but time not critical).....	60-180	120-150
5. Sparge in CO ₂ 2 to 6 hours (e.g. 3 hours).....	120-190	145-100
6. Dehydrate by heating at least 10 minutes.....	150-400	150-370
7. Filter.....	400-260	370-300

The proportions of reacting materials may vary within the ranges shown in Table II. In place of ammonia, an aliphatic amine of from 1 to 4 carbon atoms may be used. There must be present sufficient ammonia or amine so that a weight ratio of nitrogen to calcium of at least 0.02 to 1 is provided.

TABLE II

	Weight Percent	
	Broad	Preferred
Phosphosulfurized Hydrocarbon.....	17-25	19-22
Alkylated Phenol.....	5-20	6-10
Ammonium Sulfonate.....	0-5	0.5-2
Diluent Oil.....	25-60	35-45
NH ₄ OH (29% NH ₃).....	0.2-20	4-10
Water.....	0-5	0-1.5
Ca(OH) ₂ (or equivalent CaO).....	3-20	5-18
CO ₂	2-11	3-10

Preferably, the amount of carbon dioxide used is in the range of from about 80 to about 95 percent of the amount theoretically required to convert the calcium present to calcium carbonate.

The nature of this invention and the manner in which it is preferably carried out will be more readily understood from the following examples.

Example 1

A phosphosulfurized hydrocarbon was prepared on a plant scale by reacting 100 parts, by weight, of a polybutene having an average Staudinger molecular weight of about 1100, with 15 parts by weight of phosphorus pentasulfide, for 8 to 12 hours at 425-450° F. with stirring and nitrogen blowing. The phosphosulfurized polybutene had the following inspections:

Phosphorus, weight percent.....	3.45.
Sulfur, weight percent.....	6.64.
Neutralization No. to pH of 4.....	37 mg. KOH/gram.
Saponification No.....	84 mg. KOH/gram.
Viscosity at 210° F., SSU.....	20,000.

Example 2

In this example, an equivalents ratio of calcium to surfactant of about 3 to 1 was used. A blend of 536 grams of mineral oil, 279 grams of phosphosulfurized hydrocarbon made in accordance with Example 1, and 112 grams of nonyl phenol was prepared and heated to 170° F. To this blend was added a slurry of 82.5 grams of Ca(OH)₂ in 100 grams of water over a period of 20 minutes with the temperature of 170° F. being maintained. Then over a period of 80 minutes about 25,000 cc. of CO₂ (measured at 25° C.) was sparged into the mixture. The product was then dehydrated and filtered.

The process was repeated but including the step of

adding 2.4 grams of ammonium hydroxide (29% NH₃) prior to the addition of the calcium hydroxide slurry. The improvement in haze and color obtained by including the ammonium hydroxide is shown in Table III.

TABLE III

	No Ammonia	Ammonia Added
10 Haze, Nephelos ¹	47	18
Color, ASTM.....	1 1/2	1
Color, Visual Comparison.....	Dark	Light
Calcium, Wt. Percent.....	3.9	3.8

¹ Measurement made in 5 weight percent concentration in white oil.

Example 3

Using the general procedure of Example 2 but employing a calcium to surfactant equivalents ratio of 3.5 to 1, and substituting tertiary butyl amine for ammonium hydroxide, an additive was made from the following:

Mineral oil.....	520 grams.
Phosphosulfurized polybutene.....	279 grams.
Ca(OH) ₂	97 grams.
Water.....	120 grams.
25 Nonyl phenol.....	110 grams.
CO ₂	27,000 cc. (measured at 25° C.).
Tertiary butyl amine.....	6 grams.

30 The run was repeated without the added amine. The results are given in Table IV. It will be seen that haze and filter rate were greatly improved by addition of the amine.

TABLE IV

35 PREPARATION AT 3.5 TO 1 CALCIUM TO SURFACTANT RATIO

	Nitrogenous Promoter	
	None	t-butyl amine
Calcium in Product, Wt. Percent.....	4.4	5.1
40 Haze, Nephelos ¹	109	52
Filter Rate, Gal./hr./Sq. Ft.....	0.9	17.5

¹ Measurement made in 5 weight percent concentration in white oil.

Example 4

Following the preferred procedure outlined in Table 1, a detergent additive was prepared using as the feed 19.8 weight percent of the phosphosulfurized hydrocarbon of Example 1, 6.5 weight percent of nonyl phenol, 1.6 weight percent of ammonium petroleum sulfonate of about 450 molecular weight, 41.7 weight percent of a neutral mineral oil (150 SSU at 100° F.), 1.0 weight percent water, 4.4 weight percent of commercial ammonium hydroxide (29% NH₃ content), 16.0 weight percent of calcium hydroxide, and 9.0 weight percent of CO₂. The product had the composition shown in Table V. The ratio of calcium equivalents to surfactant equivalents was about 8.5 to 1.

TABLE V

	Product composition weight percent
65 Ca.....	9.0
CO ₂	12.0
Phosphosulfurized hydrocarbon.....	22.5
Nonyl phenol.....	7.4
Neutral mineral oil.....	47.4
70 Ammonium sulfonate.....	1.7

Example 5

The procedure of Example 4 was repeated with the exception that the ammonium sulfonate was omitted and the ratio of equivalents of CO₂ to calcium was varied.

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The results obtained are shown in Table VI. It will be seen that when the ammonia was omitted altogether the product was unfilterable, and therefore useless, since it is evident that the calcium carbonate was not in colloidal form. In the runs in which ammonia was used without the ammonium sulfonate, the best haze, filter rate, and odor were obtained when the ratio of chemical equivalents of CO₂ to calcium was less than 0.9. Better quality resulted when both ammonia and ammonium sulfonate were used.

TABLE VI

Nitrogenous Feed Components	CO ₂ /Ca Equivalent Ratio in Feed	Haze, Nephelos ²	Filter Rate, Gal./Hr./Sq.Ft.	Odor
Ammonium Sulfonate and ammonia. ¹	0.94	40	5.0	Mild phenolic.
Ammonia	0.99	125	1.0	Strong H ₂ S.
Do	0.94	114	1.0	Do.
Do	0.89	87	1.9	Mild phenolic.
None	0.89		Would not filter	

¹ Example 3.² Measurement made in 5 weight percent concentration in white oil.

Example 6

Again using the general procedure of Example 2 but employing a calcium to surfactant ratio of about 4 to 1, an additive concentrate was prepared from 397 grams of a 68% concentrate of phosphosulfurized polybutene in mineral oil, 112 grams of nonyl phenol, 110 grams of Ca(OH)₂, 110 grams of water, 418 grams of solvent neutral mineral oil and 30,000 cc. of CO₂ (measured at 25° C.). The process was repeated with the same ingredients in the same quantities but with the addition of 61 grams of ammonium hydroxide (29% NH₃). The haze reading for 5% concentrations of the respective products in white oil and the filtration rates of the materials during the respective preparations are shown in Table VII. It will be seen at the 4 to 1 calcium surfactant ratio, a satisfactory product was not obtained in the absence of ammonium hydroxide.

TABLE VII

EFFECT OF NH₄OH AT 4 TO 1 CALCIUM/SURFACTANT RATIO

NH ₄ OH Used	Haze (Nephelos) 5% in White Oil	Filter Rate Gal./Hr./Sq.Ft.
None	>130	4.9
2.7%	17	24.5

Example 7

To prepare an additive having a ratio of calcium to surfactant in the range of about 8 to 1, the second portion of Example 5 was repeated (i.e. using NH₄OH) except that the proportion of Ca(OH)₂ was doubled, the proportion of NH₄OH solution was increased by a factor of 1.6 and about 2.5 times as much CO₂ was employed. This gave a first product having unsatisfactory haze (130 nephelos). The preparation was repeated but in place of portions of the nonyl phenol and NH₄OH, ammonium petroleum sulfonate of about 450 molecular weight was used. The reactants were 397 grams of a 68 weight percent concentrate of phosphosulfurized polybutene in mineral oil, 91 grams of nonyl phenol, 220 grams of Ca(OH)₂, 110 grams of water, 61 grams of NH₄OH (29% NH₃), 418 grams of solvent neutral mineral oil, 41.7 grams of a 50% concentrate of ammonium petroleum sulfonate in mineral oil, and 70,200 cc. of CO₂ (measured at 25° C.). This second product had a haze of 27 nephelos (5% conc. in white oil) as compared to

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the reading of 130 in the first product preparation without the ammonium sulfonate.

Example 8

To study the effect of raising the calcium to surfactant ratios still further, products were made with ratios of 8.3, 10.2, and 13.6 using the proportions of reactants set forth in Table VIII. The haze readings on the products and the filter rates noted during the filtering step are also shown in the table. Only the product made with the 13.6 to 1 ratio was not satisfactory.

Other studies have established that a product having a haze rating of 36 nephelos can be made with a 13.4 to 1 calcium to surfactant ratio in the reactants if the preparation is done in two stages, using first an 8 to 1 calcium to surfactant ratio, dehydrating, and filtering the product before treating with additional lime, CO₂ and ammonia.

TABLE VIII

EFFECT OF INCREASING Ca/SURFACTANT RATIOS

Ratio	8.3	10.2	13.6
P ₂ S ₅ Treated Polybutene, grams (68% concentrate)	300	300	300
Nonyl phenol, grams	67	67	67
Solvent Neutral Mineral Oil, g.	312	312	312
NH ₄ OH (28% NH ₃), grams	46	46	46
Water, grams	42	80	80
Ammonium sulfonate, grams (50% concentrate, 450 M.W.)	31.2	40	31.2
CO ₂ , liters (at 25° C.)	50	64	82.5
CaO, grams	124.8	156	204
Filtration Rate, Gal./Hr./Sq. Ft.	3.6	2.8	<1.0
Product Haze, Nephelos (5% conc. in white oil)	38	91	130+

Example 9

Total water content in the reaction mixture appears to have some effect on the quality of the product at the 8 to 1 calcium to surfactant equivalents ratio as shown by the following tests. Using the technique for the preparation of the second type of product of Example 7, i.e. with ammonium sulfonate, the total water content of the feed was varied. The results shown in Table IX indicate that at the 8 to 1 calcium to surfactant equivalents ratio, the total water content of the reactants should be in the range of about 7.2 to 8.2 weight percent of the reactants.

TABLE IX

EFFECT OF WATER CONTENT IN REACTION MIXTURE

Calcium Source	Total Water Content ¹ (Percent of Feed)	Haze Nephelos ²	Filter Rate, Gal./Hr./Sq. Ft.
CaO	7.0	130+	12.2
	7.2	38	3.6
	7.5	27	4.6
Ca(OH) ₂	7.9	40	3.9
	8.0	40	5.3
	8.2	65	3.2
CaO	8.5	128	<1.0
	10.5	130+	10.0

¹ Water added plus water in Ca(OH)₂ and in NH₄OH solution (29% NH₃).² 5% solution in white oil.

Example 10

The sludge inhibiting properties of an additive of this invention in which the calcium to surfactant ratio was about 8 to 1 were studied in a low temperature engine test in which conditions were intended to simulate stop-and-go driving. A six-cylinder Ford engine was used, charged with 4 quarts of the oil under test, and run for a total of 286 hours, under the conditions given in Table X, the cycles being repeated until the end of the test.

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TABLE X

LOW TEMPERATURE ENGINE TEST CONDITIONS

	Cycle 1	Cycle 2	Cycle 3
Cycle Duration, Hours.....	1.5	2	2
Engine, r.p.m.....	500	2,000	2,000
Air-Fuel Ratio.....	11/1	13.5-14/1	13.5-14/1
Brake Horsepower Load.....	0	40	40
Torque, Pound Feet.....	0	105	105
Oil Sump Temperature, ° F.....	180±5	180±5	215±5
Jacket Water Out Temp., ° F.....	190±5	160±5	180±5

At the end of the first 66 hours, and every 44 hours thereafter, the engine was inspected by removing the oil pan, the rocker arm cover, and the push rod chamber cover, and various parts including the oil screen, the oil pan, the crankshaft, the push rod chamber, the push rod chamber cover, the rocker arm cover, and the rocker arm assembly, were rated for sludge deposition, using a demerit system in which zero represents a clean part and 10 a part covered with the maximum amount of sludge possible.

The oils tested were:

(1) Composition A, consisting of 98 volume percent of an SAE 30 grade highly refined base stock, 0.3 volume percent of a viscosity index improver, 0.7 volume percent of a zinc dialkyl dithiophosphate (C₄-C₅ alkyl groups) wear reducing agent and 1 volume percent of an additive concentrate made as described in Example 4 and containing 8.6 percent calcium.

(2) Composition B, consisting of 96 volume percent of the same base oil, 0.3 volume percent of the same viscosity index improver, and 0.7 volume percent of the same zinc dialkyl dithiophosphate, as in Composition A, plus 3 volume percent of a commercially available detergent-inhibitor comprising colloidal barium carbonate and phenate stabilized with a phosphosulfurized polybutene. The latter inhibitor contained 10.7 percent BaO; thus Compositions A and B were made up to approximately equal molar concentrations of metal.

The test results are given in Table XI.

TABLE XI
LOW TEMPERATURE SLUDGE TEST RESULTS

Hours on Test	Overall Sludge Demerits	
	Composition A	Composition B
66.....	0.06	0.14
110.....	0.16	0.32
154.....	0.25	0.63
198.....	0.31	0.81
242.....	0.53	1.21
286.....	0.78	1.47

The superiority of the additive of the present invention over the related prior art additive is readily apparent.

The additives of this invention may be incorporated in hydrocarbon oils of the general class of middle distillate fuels and lubricating oils, although their principal application is in the latter type of oils. For use in automotive crankcase lubricants, concentrations providing from 0.02 to about 0.5 weight percent of calcium are preferred. For marine diesel lubrication, concentrations providing as much as 2 weight percent calcium may be advantageous.

The oil base stock may be of any desired type, including those derived from paraffinic, naphthenic, asphaltic, or mixed base mineral crude oils by suitable refining methods. Synthetic lubricating oils of suitable viscosity may also be employed, such as di-2-ethyl hexyl sebacate, the C₁₃ oxo acid diester of tetraethylene glycol, complex esters, polyglycol type synthetic oils, and the like.

The oil compositions may contain other additives such as viscosity index improvers, e.g. polymethacrylates, polybutenes, etc., antioxidants such as phenyl-alpha-naphthylamine, alkyl phenols, bis phenols and the like, pour point depressants, dyes, antiwear agents such as zinc dialkyl dithiophosphates, other detergent inhibitors, etc.

The additives of the invention may also be used in gear lubricants, transformer oils, transmission fluids, hydraulic oils, flushing oils, industrial oils, greases, and the like.

It is to be understood that the examples presented herein are intended to be merely illustrative of the invention and not as limiting it in any manner; nor is the invention to be limited by any theory regarding its operability. The scope of the invention is to be determined by the appended claims.

What is claimed is:

1. An improved process for the preparation of a detergent inhibitor for mineral oil compositions which comprises reacting, at a temperature in the range of about 60 to 190° F. a hydrocarbon oil solution of a phosphosulfurized hydrocarbon and a phenolic compound selected from the group consisting of alkyl phenols having molecular weights in the range of 200 to 700 and sulfides of said alkyl phenols with a base selected from the group consisting of calcium oxide and calcium hydroxide, in an amount sufficient to furnish a ratio of calcium equivalents to phosphosulfurized hydrocarbon equivalents in the range of from about 3 to 1 to about 11 to 1, and thereafter with carbon dioxide, in the presence of a nitrogen base selected from the group consisting of ammonium hydroxide and aliphatic amines of from 1 to 4 carbon atoms, said nitrogen base being present in an amount to provide a weight ratio of nitrogen to calcium of at least 0.02 to 1, the amount of carbon dioxide employed being in the range of from about 80 to about 95 percent of the amount theoretically required to convert the calcium to calcium carbonate, the reaction product being dehydrated and then filtered subsequent to said treatment with carbon dioxide.

2. Process as defined by claim 1 wherein there is present in the reaction mixture up to about 5 weight percent of ammonium salt of a hydrocarbon sulfonic acid of 300 to 700 molecular weight.

3. In the preparation of a detergent inhibitor additive for mineral oil compositions by reacting, at a temperature in the range of about 60° to 190° F. an oil solution of a phosphosulfurized hydrocarbon and a phenolic compound selected from the group consisting of alkyl phenols of about 200 to 700 molecular weight and sulfides of said alkyl phenols with a base selected from the group consisting of calcium oxide and calcium hydroxide, in an amount sufficient to furnish a ratio of calcium equivalents to phosphosulfurized hydrocarbon equivalents in the range of from about 3 to 1 to about 11 to 1, and with carbon dioxide in an amount within the range of from about 80 to 95 percent of the amount theoretically required to convert the calcium to calcium carbonate, whereby a colloidal dispersion of calcium carbonate is formed, and the reaction product is dehydrated and filtered subsequent to said treatment with carbon dioxide, the improvement which comprises adding sufficient ammonium hydroxide to the reacting mixture to give a product having a haze of less than 100 nephelos when dispersed in 5 weight percent concentration in a mineral white oil.

References Cited in the file of this patent
UNITED STATES PATENTS

2,767,209	Asseff et al.	Oct. 16, 1956
2,956,018	Carlyle et al.	Oct. 11, 1960
2,989,463	Mastin	June 20, 1961
3,003,959	Wilson et al.	Oct. 10, 1961