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INCORPORATION OF ALKALI AND ALKALINE EARTH METALS IN OIL, AND RESULTING PRODUCT

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This invention pertains to a method of incorporating alkali and alkaline earth metal basic compounds such as oxides, hydroxides, and basic salts in oils, particularly oils of lubricating grade; and also concerns novel oil compositions containing such compounds.

During normal operation of internal combustion engines, acids are formed in the lubricating oil itself and in the combustion chamber. The acids formed in the lubricating oil itself are normally caused by oxidation of the lubricating oil and fuel contaminant during engine operation. The resulting organic acids and peroxides break down the lubricating oil and contribute to wear by corrosion. The combustion chamber acids normally come from the combustion products of the fuel. For example, when high sulfur fuels are used in diesel engines, sulfuric acid is formed from the sulfur. This sulfuric acid finds its way into the crankcase along with the blow-by-gases. Detergents are frequently incorporated in lubricating oil compositions for use as dispersing agents and as neutralizing agents for these acids.

The process of the present invention incorporates substantial amounts of a high quality detergent metal additive in an oil and at a relatively low cost per unit of added metal. These desirable results are achieved by first introducing into a body of such oil (advantageously in either powder form, or as an oil slurry) a basic compound of an alkali or alkaline earth metal, preferably selected from the group consisting of alkali and alkaline earth metal oxides, hydroxides, and basic salts such as carbonates. Then oxidation is accomplished by blowing gaseous oxygen (generally in air) through the resulting mixture while heating it in two temperature stages, the second stage advantageously being 50–100° higher than the first. In at least one of the stages the temperature should be at least 400° F. which is above the decomposition temperature of the metal carboxylate salts which are formed and retained at lower blowing temperatures. Such salts are well known to aggravate bearing corrosion, and their presence is minimized by the present invention. Usually the first or preheat stage is between 250 and 450° F., and the second or overheat stage should be at least 450° F. but should not generally exceed 700° F. to avoid decomposition of the oil.

The best results to date have been obtained with barium compounds, oil concentrates containing 3% or less and up to 17% Ba having been produced. A composition containing more than 3% of barium by weight is especially advantageous. However, the process is also applicable to compounds of the other alkali and alkaline earth metals, notably sodium and potassium.

We have found that a better yield of oil soluble metal compounds is obtained by conducting the oxidation in the presence of an excess quantity of the basic compounds mentioned. Such an excess assures a rapid reaction between the metallic base and the initially formed carboxylic acids (or their precursors) during oxidation, to form oil soluble metal compounds.

The presence of excess base is assured by introducing into the mineral oil an excess quantity over that which experience has indicated will be incorporated in the oil under a given set of operating conditions. Usually the excess is 20 to 100% above the amount desired, 50% being preferred. Thus, if it is desired to incorporate as high as 17% barium metal in the oil, an excess of base up to 100% would dictate the use of an amount of the basic compound wherein the barium metal is present in the amount of 34% based on the oil used. An excess of 50% would dictate the use of the basic compound wherein the barium metal is present in the amount of about 25%. To produce a concentrate having at least 3% metal incorporated therein, the basic barium compound is used in the amount wherein about 5% barium is present. After oxidation and before all the base has reacted, the crude product is filtered or centrifuged to remove the solids including the excess base.

The quantity of metal incorporated into an oil by the process described above generally is much more than would be required in the final lubricating oil itself, this being particularly true of the barium, potassium and sodium compounds. Therefore, the oil obtained as a product of the process may be considered as a concentrate when it contains more than 1% by weight of the metal 1–17% being usual; and is generally diluted with additional oil to reduce the metal to between 0.10 and 5% by weight (half or more generally being present as dispersed carbonate) before being used for lubricating an engine or other machine.

Lubricating oils in which the metal oxides, hydroxides and basic salts can be dispersed according to the present invention include a wide variety of mineral hydrocarbon oils such as naphthenic base, paraffin base, and mixed base oils. Also, synthetic hydrocarbon oils such as butylene polymer may be used. Examples of typical mineral oils of lubricating grade which have been treated by our process are the following three prepared by distillation from a paraffin base crude oil followed by furfural refining, light acid treating, clay contacting, and solvent dewaxing. The oil designations here used will be carried into the examples.

Oil	A	B	C
Viscosity, SUS at 210° F	53.2	43.3	65.4
Flash Point, COC, ° F	445	415	465
Gravity, ° API	29.3	31.7	20.1
Sulfur content, wt. percent	0.36	0.11	0.20
Ash, wt. percent	0.001	0.001	
Viscosity Index			90

In carrying out the process described above, it has been found that excellent results are obtained by maintaining the temperature between 300 and 450° F., with the first stage near the lower value and the second stage near the higher. At least the second stage should be above 400° F., as mentioned previously. The higher the temperature the more rapid is the reaction, and the greater is the amount of barium or other metal incorporated in the oil. For example, at a temperature of 400° F. six hours of air blowing were required to incorporate about 2.5% of barium in mineral oil A, whereas at 450° F. only one hour was required for the same result in one stage operation. Excellent results have been obtained by blowing with air for more than 2 hours at 350° F. followed by heating to 450° F. with continued air blowing, and then, if desired, air blowing for up to 1 hour at 450° F.

It should also be noted that the amount of barium or other metal incorporated by our process increases with the time of oxidation as well as with the temperature. For example, in one-stage operation, at 450° F. two hours of oxidation resulted in a little less than 4% of barium being incorporated, whereas more than 6% of barium was incorporated in four hours.

Generally our novel process is carried out by blowing air throught the mineral oil so that the oxygen content

effects the necessary reaction even though diluted with atmospheric nitrogen. However, it is to be understood that oxygen can be passed through as substantially pure oxygen or ozone; or either form in mixture with other gases, and in the same or other proportions than in air. The term "oxygen" as used herein is intended to embrace any of the foregoing conditions.

When the metal compounds have been dispersed in mineral oil by our novel process and excess solids have been filtered out, the resulting oil concentrate composition generally is clear, filterable, and stable. The metal is then present substantially as a dispersion of its carbonate in the oil, rather than as carboxylate salts which result both from the addition of the metal hydroxide to an oil subsequent to air blowing, and from air blowing at too low a temperature.

Other supplemental additives may be used in the final lubricating oil compositions. The lubricating oil compositions may contain oxidation inhibitors, such as organo esters of phosphorus (e.g., zinc dithiophosphate and calcium dithiophosphate); metal salts of thiocarbamic acids (e.g., zinc dibutyl dithiocarbamate); sulfides (e.g., sulfurized olefins, or P_2S_5-pinene reaction products, etc.); amines (phenyl alpha naphthyl amine; 1,4-diamino (dodecyl) anthraquinone; p,p'-dioctyl diphenyl amine; N-diethyl thiocarbamyl-p-phenylene diamine, etc.).

Furthermore, the final lubricating oil compositions may contain pour point depressants, corrosion inhibitors, oiliness agents, extreme pressure agents, blooming agents, compounds for enhancing the viscosity index of hydrocarbon oils; grease-forming agents, other dispersants, etc.

The following examples illustrate the effectiveness of our process for introducing metal compounds into mineral oils. Except where stated otherwise, heating from the first stage oxidation temperature to the second stage oxidation temperature was as rapid as possible, normally requiring 10 to 20 minutes.

EXAMPLE I

1,285 grams of anhydrous barium hydroxide were mixed with 10 kilograms of oil C and, while stirring, air was then blown throught the mixture at a rate of 15 liters per minute (l./min.) for six hours while the temperature of the oil was maintained at 350° F. The mixture was then heated rapidly over 25 minutes to 450° F. while air blowing was continued. After cooling and filtering the resulting concentrate product was found to contain 3.2% of barium and 0.29% carbon dioxide and had a Neut. No. (alkaline) of 4.4.

CFR engine test

23.7 parts by weight of this product were then blended with 76.3 parts of oil A and the resulting lubricant containing 0.76% of barium was tested in the CFR (Cooperative Fuels Research) engine low temperature ring wear test in comparison with base oil A. This test measures the amount of protection afforded by an oil against corrosion wear caused by low temperature operating conditions. The CFR engine test was performed in a CFR single cylinder 3¼ x 4½ internal combustion engine having a cast iron piston and babbitt metal bearings, operating at 900 r.p.m. The oil pressure was about 20 p.s.i. and the oil temperature in the sump was about 120° F. The temperature of the cooling water was 80° F. at discharge. It was found that the weight loss of the top compression ring after 20 hours was reduced by 59% compared to the base oil.

Supercharged caterpillar engine test ST1

The same concentrate was also blended with a 70 viscosity index residual distillate base oil and other additives to provide a lubricating oil containing 16.7% by weight of concentrate (which provides 0.54% of barium), 2.0% by weight of normal calcium petroleum sulfonate concentrate, and 1.2% by weight of a neutral terpene-P_2S_5 reaction product. This lubricating oil was then tested for engine cleanliness for 50 hours in the supercharged caterpillar engine test ST–1 (supercharge pressure 45 in Hg absolute) in a single cylinder caterpillar diesel engine having an aluminum alloy piston with 3 compression and 1 oil rings operating at 900 r.p.m. at a load of about 33 brake horsepower, a jacket temperature of 155–195° F. and an oil temperature in the sump of 200° F., and an oil pressure of 30 p.s.i.

When burning a fuel containing 0.6% of sulfur in the engine, the lubricating oil afforded a piston demerit rating of only 28, based on the piston cleanliness, compared to 75 for the piston with the base oil alone, 70 for the piston with the base oil plus 2% by weight of the same normal calcium petroleum sulfonate concentrate, and 53 for the piston with the base oil containing both 2% of the same normal calcium petroleum sulfonate concentrate and 1.2% of the same neutral terpene-P_2S_5 reaction product concentrate.

EXAMPLE II

918 grams of barium oxide and 108 ml. of water (to hydrate the barium oxide) were mixed with 3000 grams of oil B and then blown with air flowing at 10 l./min. for six hours at 350° F. while stirring. A sample of the product was then taken, filtered, and found to contain 1.26% of barium. The rest of the product was then heated to 450 ° F. during one hour while continuing the air blowing, after which the product was found to contain 4.90% of barium after filtering.

EXAMPLE III

459 grams of barium oxide and 54 ml. of water (to hydrate the barium oxide) were mixed with 3000 grams of oil A and then blown with air flowing at 10 l./min. for three hours at 350° F. while stirring. A sample of the product was then taken, filtered, and found to contain 0.88% of barium. The rest of the product was then heated to 450° F. during one hour while continuing the air blowing, after which the product was found to contain 5.34% of barium after filtering.

EXAMPLE IV

307 grams of barium oxide were mixed with 1000 grams of oil C and blown for four hours at 350° F. with air flowing at 10 l./min. while stirring. The product was then heated rapidly to 400° F., blown for 30 minutes at this temperature, and then found to contain 3.32% of barium after filtering.

EXAMPLE V

459 grams of barium oxide and 54 ml. of water were mixed with 2700 grams of oil B and 300 grams basic barium petroleum sulfonate and blown for one hour at 350° F. with air flowing at 10 l./min. The product was then heated over a period of one hour to 450° F., held one hour at 450° F., filtered, and then found to contain 4.53% of barium.

The run was repeated with the same conditions except that the oxidizing time was two hours at 350° F. The final product then contained 10% of barium.

EXAMPLE VI

148 grams of calcium hydroxide was mixed with 1000 grams of oil A and blown for six hours at 350° F. at an air rate of 10 l./min. while stirring. Then the mixture was rapidly heated to 450° F. and held for one hour at this temperature while continuing the blowing with air. After filtering, the product was found to contain 0.23% of calcium.

EXAMPLE VII

168 grams of calcium oxide and 54 grams of water were mixed with 2700 grams of oil A together with 300 grams of basic calcium petroleum sulfonate (as a dis-

persing agent.) After blowing with air at 10 l./min. for three hours at 350° F. a filtered sample contained 0.57% of calcium. The temperature was then raised over one hour to 450° F. with continued blowing, at which time a filtered sample contained 0.78% calcium.

EXAMPLE VIII

121 grams of magnesium oxide, 300 grams of basic magnesium petroleum sulfonate (as a dispersing agent), and 54 ml. of water were mixed with 2700 grams of oil A and blown with air at 10 l./min. for 3 hours at 350° F. Then the temperature was raised over one hour to 450° F. with continued blowing which continued for one hour at 450° F. Upon filtering, the product filtrate was found to contain 0.37% of magnesium.

EXAMPLE IX

396 grams of 85% potassium hydroxide and 820 grams of sulfonic acid concentrate in petroleum ether solution (36.6% stripping residue, having a Neut. No. of 36.4) were mixed with 2700 grams of oil A heated to distill the petroleum ether solvent, and blown with air at 10 l./min. for three hours at 350° F. after which a filtered sample contained 3.5% potassium. After continued heating and air blowing for one hour to a temperature of 450° F. and for one hour at 450° F. a filtered sample contained 5.2% potassium and 1.88% carbon dioxide.

EXAMPLE X

120 grams of sodium hydroxide (pellets) were mixed with 300 grams of a soluble sodium petroleum sulfonate concentrate (3% sodium; mol. wt. 450) and 2700 grams of oil A. The reaction mixture was heated to 350° F., while stirring and blowing with air at the rate of 10 l./min. and oxidation was continued while heating at 350° F. for three hours. The temperature was then raised slowly to 450° F. over one hour and oxidation continued for one hour at 450° F. The filtered product was clear and fluid and contained 1.6% sodium and 0.85% carbon dioxide by analysis and had an alkaline Neutralization No. 8.5.

EXAMPLE XI

458 grams of barium oxide were mixed with 2700 grams of butylene polymer and 54 ml. water and, while stirring, air was blown through the mixture at a rate of 10 l./min. while heating to 350° F. Then 300 grams of basic barium petroleum sulfonate (11% Ba) was added and the oxidation was continued three hours at 350° F. The temperature was then gradually raised over one hour to 450° F. and oxidation continued for one hour at 450° F. The filtered product contained 16.6% Ba by weight.

Physical tests characterizing the polybutylene polymer charged above include:

Flash, Cleveland open cup, ° F	240
Viscosity, SSU at 100° F	111.5
Viscosity, SSU at 210° F	40.6
Mol. wt	324

EXAMPLE XII

307 grams barium oxide were mixed with 1000 grams of a naphthene base oil (having a viscosity of 46.5 SSU at 210° F. and 311 SSU at 100° F.), and 36 ml. water. The reaction mixture was heated to 350° F., while stirring and blowing with air at the rate of 10 l./min. and oxidation was continued for six hours at 350° F. The temperature was then rapidly raised to 400° F. and oxidation continued for 15 min. at 400° F. The filtered product analyzed 3.7% Ba by weight.

The mechanism of the reaction according to our invention is not completely understood, but present evidence suggests that the overall reactions may be summarized as consisting of (1) oxidation and formation of sparingly soluble barium or other metal soaps, and (2) decarboxylation of the metal soaps to yield an oil dispersable form of barium or other metal carbonate. Apparently the synthesis is favored by conducting a primary oxidation at the lower temperature such as 350° F., during which soap formation is the predominant process, followed by an overheat oxidation at about 450° F. during which both decarboxylation and soap formation occur.

This application contains subject matter in common with application Serial No. 645,673 filed concurrently herewith by Kreuz, Wiley and Givens entitled "Process For Incorporating Compounds of Barium in Oil, And The Resulting Product." It also contains subject matter in common with application Serial No. 645,667, now abandoned, filed concurrently herewith by Kluge, Kreuz and Wiley, entitled "Oil Containing Alkali and Alkaline Earth Metal Basic Compounds, And Process For Producing Same."

Obviously, many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. A process for preparing a detergent concentrate which comprises providing a mixture consisting essentially of a hydrocarbon lubricating oil, selected from the class consisting of mineral lubricating oils and alkylene polymer oils, and a basic metal compound selected from the class consisting of alkali metal and alkaline earth metal oxides and hydroxides in an amount sufficient to provide about 5–34 percent by weight of metal in the said mixture, heating the said mixture at a temperature of at least about 300° F. but below 400° F. for at least 2 hours, thereafter heating the said mixture to a higher temperature in the range 400–700° F. but below the decomposition temperature of the said lubricating oil while blowing air through the said mixture at a rate of at least about 0.09 liter of air per hour per gram of the said lubricating oil during the said heating, and separating any unreacted basic metal compound from the resulting product.

2. The process according to claim 1 wherein the said mixture is heated at a temperature of about 350° F. for at least about 3 hours and at a temperature in the range 400–450° F. for at least 30 minutes.

3. The process according to claim 1 wherein the said metal is barium.

4. The detergent concentrate obtained by the process of claim 1 containing about 1–17 percent by weight of metal.

5. A lubricating composition comprising a lubricating oil in major proportion and a minor proportion of the detergent concentrate of claim 4, sufficient to provide about 0.10–5 percent by weight of metal in the said lubricating oil.

6. The detergent concentrate of claim 4 wherein the said metal is barium.

References Cited in the file of this patent

UNITED STATES PATENTS

2,008,490	Dietrich	July 16, 1935
2,055,043	Nelson	Sept. 22, 1936
2,079,051	Sullivan et al.	May 4, 1937
2,274,057	Gerlicher	Feb. 24, 1942
2,417,428	McLennan	Mar. 18, 1947
2,430,864	Farkas et al.	Nov. 18, 1947
2,447,794	Brewer	Aug. 24, 1948
2,779,737	Koft	Jan. 29, 1957
2,895,978	Brooks	July 21, 1959
2,955,084	Bartleson et al.	Oct. 4, 1960