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OIL DISPERSIBLE INORGANIC BORATE IN COMBINATION WITH EP AGENTS AS LUBRICATING OIL ADDITIVES

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U.S. Cl. 252—25 6 Claims

ABSTRACT OF THE DISCLOSURE

Oil dispersible hydrated alkali metal borate antiwear additives are combined with sulfur or halogen containing extreme pressure additives to provide compositions having excellent wear and extreme pressure properties while not contributing to inorganic salt deposition resulting from contact with moisture.

BACKGROUND OF THE INVENTION

Field of the invention

U.S. Pat. No. 3,313,727, issued Apr. 11, 1967, disclosed novel hydrated amorphous alkali metal borates which were oil dispersible and had excellent extreme pressure (EP) and antiwear properties. It was found, however, that to obtain the desired properties, relatively high concentrations of the alkali metal borates were required, e.g., at least 5 percent and usually from about 10 to 15 weight percent of the total composition.

At these concentrations, the hydrated alkali metal borates were found to be water sensitive. In moisture corrosion tests simulating axle operation, substantial quantities of white deposits (crystalline hydrates) were found on the bearings and races. Therefore, unless strict moisture control was maintained, the buildup of inorganic deposits obviated the use of the borates.

Description of the prior art

As already indicated, U.S. Pat. No. 3,313,727 discloses alkali metal borates as EP additives to lubricants. Numerous patents and articles have issued disclosing sulfur-containing organic compounds as EP agents. See, for example, an article by W. T. Stewart and F. Stuart in "Advances in Petroleum Chemistry and Refining," 7, 3 beginning at page 34 and articles cited therein.

Numerous patents have issued on sulfur-containing organic compounds for use as EP agents, such as U.S. Pat. Nos. 2,110,281; 2,205,858; 2,330,858; 2,526,041; 2,528,773 and 2,653,910. These patents include sulfurized hydrocarbons, such as polyisobutylene, thienyl derivatives, and trithiones.

Other compositions which have found use are those which combine both sulfur and halogen, particularly chlorine, as illustrated in U.S. Pat. Nos. 2,156,265; 2,244,886; 2,298,639; 2,503,290; 2,546,941 and 3,268,449. These compositions include chlorinated and sulfurized hydrocarbons, sulfochlorinated alkylarenes, hexachlorothiolane, and reaction products of sulfur dichloride and halogenated arenes in the presence of a Friedel-Crafts catalyst.

Finally, EP agents which are chlorinated hydrocarbons may also be used. These include chlorinated wax, olefins or naphtha, with chlorine contents in the vicinity of about 40 weight percent. See, for example, U.S. Pat. Nos. 2,850,452; 2,921,902; and 2,932,615.

SUMMARY OF THE INVENTION

This invention concerns the use in a lubricating oil of an oil dispersible alkali metal borate hydrate at low concentrations with a sulfur or chlorine-containing extreme pressure (EP) additive to obtain a lubricating oil having wear and extreme pressure properties far superior to the properties of the extreme pressure additive.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The compositions of this invention have a hydrocarbon medium, an oil dispersible alkali metal borate hydrate to be described subsequently and a sulfur or chlorine-containing extreme pressure additive. The amount of the borate and extreme pressure additive present in the composition will be from about 0.9 to 4.0 parts of the borate additive and from 2.5 to 10 parts of the extreme pressure additive per 100 parts of composition, more usually from about 1 to 3.5 parts and 3 to 8 parts, per 100 parts of composition. The amount of each additive and ratio will be optimized to obtain optimum performance for minimum cost and additive.

Other additives may also be present in the compositions, such as anti-rust additives, antioxidants, detergents, viscosity index improvers, anti-foaming agents, pour point depressants, etc. These additives will generally not exceed a total of 10 weight percent of the composition.

ALKALI METAL BORATE HYDRATES

The alkali metal borate hydrates which find use in this invention are extensively discussed and claimed in U.S. Pat. No. 3,313,727. There is no need to repeat the disclosure of that patent, and only the highlights will be indicated.

The alkali metal borates which find use are the metaborates and tetraborates of sodium and potassium having from 0.9 to 4 waters of hydration, i.e., sodium metaborate, potassium metaborate, sodium tetraborate, potassium tetraborate or mixtures thereof, dispersed in oil by means of a lyophilic surface active agent. The preferred compositions are the sodium metaborates and potassium tetraborates having from 1.5 to 2.5 waters of hydration. These compositions have the formula:

$$M_2O \cdot mB_2O_3 \cdot nH_2O$$

wherein M is an alkali metal of atomic number in the range 11 to 19; m is a number of from 1 to 2 and n is a number of from 0.9 to 4.

In preparing the alkali metal borates, a wide variety of emulsifying agents or dispersants may be used. The surface active agents are referred to as lyophilic surface active agents. Of the two major classes, the ionic emulsifying agents are the metal salts of oil-soluble acidic organic compounds, e.g., sulfonates, carboxylates, phenates

and quaternary ammonium salts. The neutral or non-ionic surface active agents are exemplified by alkenyl succinimides, aliphatic amine amides of maleic anhydride modified hydrocarbon polymers and addition polymerizable copolymers of acrylates and amides.

The preferred dispersants are the lyophilic ionic surface active agents, such as the carboxylates, phenates and sulfonates of alkaline earth metals, e.g., calcium and barium.

In preparing the alkali metal borates, about 0.05 to 0.5 part, more usually from about 0.1 to 0.3 part of emulsifier will be used per part of borate salt.

The borate compositions are prepared by dehydrating a water in oil emulsion of an aqueous solution of an alkali metal borate, providing the desired dispersion of the hydrated alkali metal borate in the oil medium. The alkali metal borate, water and the desired emulsifier are introduced into an inert non-polar medium, the medium vigorously agitated to provide a dispersion of the water in the non-polar medium and then the mixture heated at a temperature and for a time which provides the desired degree of hydration of the alkali metal borate. Conveniently, the borate may be added as an aqueous solution to the oil. Also, antifoaming agents may be added, generally in from about 0.00005 to 0.005 weight percent of the total composition.

The temperature at which the emulsion is heated will generally be at least 250° F., more usually at least 300° F. Lower temperatures may be used at reduced pressures. However, the process is conveniently carried out at atmospheric pressures and at temperatures above the boiling point of water.

The resulting alkali metal borate hydrate dispersion is a stable dispersion in a hydrocarbon medium of amorphous or glassy particles, almost all of which are less than about 1μ in size. The particles are alkali metal meta- or tetraborates, having from about 0.9 to 4, more usually 1.5 to 2.5 waters of hydration.

The following example is illustrative of the method of preparation of the alkali metal borates.

A blend of 83 parts by weight of SAE 90 base oil, 2 parts of neutral calcium petroleum sulfonate (1.67 percent calcium) and 0.001 part dimethylsilicone of 350 cs. (anti-foaming agent) was placed in a 1-quart container of a Waring Blendor equipped with a heating jacket and heated to 200° F. with stirring. A solution of 15 parts of sodium metaborate octahydrate ($Na_2O \cdot B_2O_3 \cdot 8H_2O$) dissolved in 15 parts of water, also at 200° F., was added gradually with continuous, vigorous blending and the resulting emulsion was partially dehydrated by heating to 300° F. in 25 minutes with continuous, vigorous stirring. A stable dispersion was obtained containing 9.56 weight percent of a glass of the composition:

$$Na_2O \cdot B_2O_3 \cdot 1.84H_2O$$

EXTREME PRESSURE AGENTS

The mechanism of extreme pressure dopes is described in Zuidema, "Performance of Lubricating Oils," 2nd ed., Reinhold Pub. Corp., New York, 1959. One page 11, the mechanism is described as follows: "In the case of chlorinated and sulfurized EP dopes, the mechanism has been quite well established as consisting of the formation of an inorganic film. Baxter, Snow and Pierce show that pretreatment of the test pieces with chlorinated or sulfurized EP dope at elevated temperatures or with hydrochloric acid resulted in a considerable increase in breakdown load in both the 4-ball and the Timken tests.

"Davey found that pretreatment of the test pieces used in the 4-ball apparatus with free sulfur or with ammonium sulfide, both of which gave sulfide films, resulted in families of friction time curves for straight mineral oils, at least until the sulfide film was worn away, similar to those obtained when a sulfur containing EP oil is run with untreated steel balls."

While sulfur-containing EP additives may respond in different ways depending on how the sulfur is incorporated in the organic compound, basically the sulfur-containing dopes are sources of sulfur and the chlorine-containing dopes are sources of hydrogen chloride. Since the sulfur and chlorine-containing EP additives are primarily sources of sulfur or hydrogen chloride for reacting with the iron present in the gears, a wide variety of EP additives may be used.

Illustrative of the sulfur-containing EP additives, either containing sulfur by itself or in combination with chlorine are olefin-sulfur copolymers, e.g., isobutylene sulfur copolymer, sulfurized hydrocarbons, chlorinated and sulfurized hydrocarbons, disulfides, trithione, hexachlorothiolane, etc. Any sulfur-containing extreme pressure additive may be used which provides sulfur in a form which will react with the metal gear to form a soft layer and prevent scuffing, galling and seizing.

Among the chlorinated extreme pressure agents are chlorinated hydrocarbons, such as chlorinated waxes, olefins, low molecular weight polymers, e.g., polyethylene or polyisobutylene, and naphthas. For chlorinated extreme pressure agents, it is necessary that the compound be a source of acidic chloride and not interfere with the proper functioning of the lubricating oil.

The extreme pressure additives which may be used in this invention are composed solely of carbon, hydrogen, sulfur and chlorine, although not necessarily all of them. The compounds may include aliphatic, alicyclic and aromatic groups. Heterocyclic groups may also be present with sulfur as the annular heteroatom.

OIL MEDIA

The oil media can be any non-polar fluid medium of low dielectric constant which is inert and of lubricating viscosity. Fluids of lubricating viscosity generally have viscosities of from 35 to 50,000 Saybolt Universal seconds (SUS) at 100° F. (V_{100}).

The fluid medium or oil may be derived from either natural or synthetic sources. Included among the natural hydrocarbonaceous oils are paraffin base, naphthenic base, asphaltic base and mixed base oils. Synthetic oils include polymers of various olefins, generally of from 2 to 6 carbon atoms, alkylated aromatic hydrocarbons, etc. Non-hydrocarbon oils include polyalkylene oxide, e.g., polyethylene oxide, aromatic ethers, silicones, etc.

The preferred media are the hydrocarbonaceous media, both natural and synthetic.

EXAMPLES

In order to demonstrate the effectiveness of the compositions of this invention, an exemplary alkali metal borate hydrate, prepared as previously described, was employed at concentrations at which it, by itself, was an unacceptable additive. The alkali metal borate hydrate was combined with exemplary sulfur or chlorine-containing extreme pressure additives; namely, poly(isobutylene sulfide) (supplied as Anglamol 32, by Lubrizol Corp. contains ~46 percent S), dibenzyl disulfide, and polychlorinated wax (supplied as Unichlor 40 by U.C.C.).

The following table indicates the compositions prepared, the concentrations of the individual components, and the results of the SAE EP test described in Federal Test Method Standard No. 791a, dated Dec. 30, 1961, Method 650.1; the SAE wear test (4 hours at 180 lbs. and 500 r.p.m.) and the 4-ball wear test, reported as scar diameter, where the conditions are 0.5 hour, 70 kg. and 1200 r.p.m.

The results for the compositions of this invention are compared with the results when using individual components. The following table provides the results.

TABLE I

Composition [1]						
Alkali metal borate [2]	Wt. percent	Extreme pressure additive [3]	Wt. percent	SAE EP, lbs.	SAE wear, mg.	4-ball wear, scar diameter, min.
I	1			115	4	
I	3			145	<5	
		A	5	500+	2,541	
		A	4	343	1,912	
I [4]	1	A	3	500+	24	0.51
I	1	A	5	500+	15	0.52
		B	3.3	110	1,147	
I	1	B	3.3	190	10	
		C	4	133	635	
I	1	C	4	385	9	
I	3	C	4	500+		

[1] Base oil: 35 wt. percent 230 bright stock; 35 wt. percent 210 bright stock; 30 percent 130 neutral oil.

[2] I—$NaBO_2 \cdot 0.92H_2O$ (approx.). Sodium metaborate tetrahydrate emulsified with calcium sulfonate derived from 480 neutral oil (1.67% Ca) and dehydrated at 400° F. (The weight ratio of hydrated borate to emulsifier is 0.22:1.)

[3] A—poly(butene sulfide); B—dibenzyl disulfide; C—Unichlor 40.

[4] Contains 0.25 weight percent of neutral calcium sulfonate which contains 2 percent of a polypropylene glycol rust inhibitor.

It is evident from the above table that the products of this invention impart excellent extreme pressure properties to the lubricating oil as well as significantly prevent wear. Furthermore, in the moisture corrosion test (Federal Test Method Standard No. 5326) in 7 days for a 5 percent poly(isobutylene sulfide)-1 percent

$$K_2O \cdot 2B_2O_3 \cdot H_2O$$

composition, only a very slight trace of rust and deposits on the bearing were found, while with the composition containing the 3 percent poly(isobutylene sulfide) and 1 percent sodium metaborate, only trace deposits on the race and cage were found.

Thus, while still retaining the excellent antiwear and extreme pressure properties which were found with the alkali metal borate compositions at the relatively high concentrations, the problem of inorganic deposits in the presence of moisture is avoided. The subject compositions of this invention can, therefore, be used where the presence of moisture cannot be prevented.

As will be evident to those skilled in the art, various modifications on this invention can be made or followed, in the light of the foregoing disclosure and discussion, without departing from the spirit or scope of the disclosure or from the scope of the following claims:

What is claimed is:

1. A lubricating oil composition having per hundred parts from 0.9 to 4.0 parts of a hydrated alkali metal borate of the formula:

$$M_2O_2 \cdot mB_2O_3 \cdot nH_2O$$

wherein M is an alkali metal of atomic number 11 to 19, m is a number of from 1 to 2, and n is a number of from about 0.9 to 4, wherein the hydrated alkali metal borate is in the form of amorphous particles of less than about 1μ in size and from 2.5 to 10 parts of a sulfurized and/or halogenated hydrocarbon extreme pressure additive.

2. A composition according to claim 1, wherein said alkali metal borate is sodium metaborate.

3. A composition according to claim 1, wherein said alkali metal borate is potassium tetraborate.

4. A composition according to claim 1, wherein said extreme pressure additive is poly(isobutylene sulfide).

5. A composition according to claim 1, wherein said extreme pressure additive is dibenzyl sulfide.

6. A composition according to claim 1, wherein said extreme pressure additive is chlorinated wax.

References Cited

UNITED STATES PATENTS

2,932,615	4/1960	Jordan et al.	252—45
2,987,478	6/1961	Matson	252—46.4
3,103,494	9/1963	Spengler et al.	252—46.4
3,313,727	4/1967	Peeler	252—25

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,565,802 Dated February 23, 1971

Inventor(s) WILLIAM W. WEST ET AL.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Col. 3, line 61, "One" should read --On--.

Col. 5, line 50, "$M_2O_2 \cdot mB_2O_3 \cdot nH_2O$" should read

--$M_2O \cdot mB_2O_3 \cdot nH_2O$--.

Signed and sealed this 22nd day of June 1971.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
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Commissioner of Patents