United States Patent Office 2,721,846 Patented Oct. 25, 1955

2,721,846

FLUSHING OIL COMPOSITION

Joseph F. Lyons, Wappingers Falls, and Theodore C. Heisig, White Plains, N. Y., assignors to The Texas Company, New York, N. Y., a corporation of Delaware

No Drawing. Application April 30, 1953, Serial No. 352,282

8 Claims. (Cl. 252—49.6)

This invention relates to an improved lubricating composition for use as a flushing oil. More particularly, this invention discloses a flushing oil possessing excellent anti-rust, antioxidant and drying properties and an improved flash point over presently known flushing oil compositions.

Flushing oils find application in the periodic cleansing of internal combustion engines, turbines and the like to remove acidic and sludge-like materials and in the reactivation of mechanisms which have been protected in storage by the application of preservative compounds. This latter utilization of flushing oils has been particularly important in recent years in reactivating military equipment which has been in storage since World War II. It is important that flushing oils, which are used either for periodic removal of sludge deposits from engines or turbines or for the reactivation of stored mechanical equipment, be characterized by anti-rust and antioxidant properties and by the ability to remove moisture or oil-water emulsions from the equipment. This latter property, namely, the ability to remove water or oil-water emulsions, is normally termed a drying property. This drying property is of prime importance in the formulation of a good flushing oil because water and oil-water emulsions are often encountered in overhaul of power plants and in the reactivation of engines and turbines which have been protected in storage with preservative compounds.

The flushing oils of this invention comprise a mineral oil as a major constituent, 0.001 to 2.0 weight per cent oil-miscible aliphatic dicarboxylic acid having at least 10 carbon atoms, 0.0001 to 1 weight per cent of an oil-miscible aliphatic acid phosphate, 0.05 to 3.0 weight per cent of an oil-miscible alkylated phenol and 4 to 10 weight per cent tripropylene glycol monomethyl ether. Ordinarily, the flushing oil also contains 0.0001 to 0.002 weight per cent of a polymeric organic silicone.

At the present time, monoalkyl ethers of ethylene glycol and polyethylene glycols are used to impart drying properties to flushing oils. The use of these materials to enhance the drying properties of the flushing composition has the serious drawback that the flash point of the resulting mixture is substantially reduced with an accompanying increase in fire hazard. The novel flushing oils of this invention possess excellent drying, anti-rust and antioxidant properties, and, in addition, have improved flash points.

Flushing oils of the prescribed composition perform well in removing sludge deposits in periodic overhauls and in removing corrosion-preventing preservative compounds from stored mechanical equipment. In addition, they pass the moisture removability and flash point specifications prescribed by the military for compounds to be

used in reactivation of stored equipment. The flushing oils of this invention have flash points which are about 25° F. higher than are possessed by any known oils having equivalent drying, anti-rust and antioxidant properties.

The oil-miscible dicarboxylic acids of the invention may be any aliphatic dicarboxylic acid which contains at least 10 carbon atoms in the molecule and at least one carbon atom between the carboxyl groups. Typical examples of the preferred acids are the alkyl maleic acids, alkenyl succinic acids, and alkyl citraconic acids.

The amounts in which the dicarboxylic acids are incorporated in an oxidation-inhibited lubricating composition, or combined with an oxidation inhibitor and then incorporated in a lubricant, will vary in accordance with the type of inhibitor and the lubricating oil to which they are added. In general, the dicarboxylic acid is incorporated in the lubricating oil in amounts ranging between 0.001 and 2.0 per cent by weight. The preferred concentration of dicarboxylic acid is between 0.01 and 0.5 weight per cent.

Alkenyl succinic acids are the preferred dicarboxylic acids for use in this invention. The preparation of the alkenyl succinic acids is carried out by condensation of maleic acid anhydride with an olefin or mixtures thereof, either straight or branched chain, which contains an average of at least 6 carbon atoms and preferably 10 or more. These olefins may be obtained from any of the usual sources, such as vapor phase cracking of petroleum oil or wax, the polymerization of lower molecular weight olefins and fractionation of Fischer-Tropsch product. This condensation reaction, followed by hydrolysis, produces dicarboxylic acids which may exist as an alkyl maleic acid, an alkenyl succinic acid, or mixtures thereof. In order to simplify the description of the acids produced by this reaction, reference will be made throughout the specification and claims to alkenyl succinic acids.

The second component of the flushing oil, namely, the aliphatic acid ester of a phosphorus acid, embraces any aliphatic ester of a phosphorus acid which contains at least one replaceable hydrogen linked to the phosphorus through an oxygen atom, and which is soluble or miscible in the lube oil fraction. The acids of phosphorus whose aliphatic acid esters satisfy the requirements of the present invention are the various phosphoric acids, which include the ortho, meta and pyro acids, together with the polymeric forms thereof. The aliphatic group, which comprises both alkyl and alkenyl radicals, must be sufficiently aliphatic in nature and of such molecular weight as to render the compound either soluble or miscible in the lube oil fraction; a minimum of at least 10 aliphatic carbon atoms is required. Examples of the type of compounds falling within this classification which have been found satisfactory for use in the inhibitor combination are the following: dilauryl acid pyrophosphate, n-butyl oleyl acid orthophosphate, monolauryl acid orthophosphate and butenyl lauryl acid orthophosphate. Aliphatic acid phosphates may be prepared by any of the known methods of synthesis and may consist of mixed alkyl esters, such as butyl lauryl acid orthophosphate or mixtures of mono- and di-substituted esters, such as mono- and di-lauryl acid orthophosphate, as well as the simple esters, such as mono-lauryl acid orthophosphate. The aliphatic acid phosphate constitutes 0.0001 to 1.0 weight per cent of the total flushing oil; the preferred concentration falls between 0.001 and 0.03 weight per cent.

Normally, alkenyl succinic acid and the aliphatic acid phosphate are combined to form a concentrate comprising approximately 6 parts of alkenyl succinic acid and 1 part of aliphatic acid phosphate. A concentrate which possesses superior anti-rust properties comprises approximately 45.5 weight per cent C_{18} alkenyl succinic acid, 7.5 per cent dilauryl acid orthophosphate and 47 per cent lube oil.

The oil-miscible alkylated phenols employed in the flushing oils of this invention impart antioxidant properties thereto. It is important that there be sufficient carbon atoms in the alkyl groups attached to the benzene ring that the alkyl phenol be oil-soluble. The preferred alkyl phenols are tri-alkylated compounds having tertiary alkyl groups in the 2 and 6 position such as 2,4,6-tri-tertiary butyl phenol and 2,6-isopropyl-4-ethyl phenol. A particularly effective compound of this type is 2,6-di-tertiary butyl-4-methyl phenol which is sold commercially under the trade name "Paranox 441." The flushing oils of the invention contain 0.05 to 3.0 weight per cent alkylated phenol with the preferred concentration range falling between 0.1 and 1.5 per cent.

The incorporation of an organic silicone in the flushing oils suppresses the foam-forming tendencies of the oil. These organic silicones may be obtained by hydrolysis of the dialkyl or mixed alkyl-aryl silicon dichlorides which are prepared by a Grignard reaction using alkyl or mixtures of alkyl and aryl magnesium bromides and silicon tetrachloride, and the silicols thus formed dehydrated by heat treatment. This product may be further polymerized by additional heat treatment, and organic silicones of varying degrees of polymerization and molecular weight may be obtained by varying the time and temperature of the heat treatment.

The organic silicones, and particularly the dimethyl silicones, are usually oil-insoluble and are incorporated in the lubricating oil by means of a kerosene concentrate. Normally, the kerosene concentrate contains 5 to 15 weight per cent silicone; the concentrate used in formulating flushing oils of this invention comprises 12 weight per cent silicone. To obtain foam-inhibiting properties, very small amounts of the silicone need be incorporated in the oil and these amounts usually range between 0.0005 and 0.01 per cent by weight of the lubricating oil.

The drying agent which effects a substantial improvement in the flash point of the flushing oils of this invention without sacrificing the moisture removing properties of the flushing oil is monomethyl ether of tripropylene glycol. The flushing oil normally contains between 4 and 10 per cent of tripropylene glycol monomethyl ether with 5 to 8 per cent being the preferred concentration of the drying agent.

Although the lubricating oil component of the flushing oil can be either a paraffin base or a naphthene base oil, it has been found that naphthene base oils are preferred because they possess better solvent powers for preservative agents used during storage of engines, turbines and the like. The lube oil fraction employed should be of low viscosity in order to possess solvent powers required in an oil of this type. It is possible to add a high boiling gas oil fraction such as kerosene to the lube oil fraction in order to enhance the solvent properties of the flushing oil composition. The SSU viscosity at 100° F. of the hydrocarbon fraction employed in the flushing oil of this invention, whether it be a paraffin or naphthene base, should fall between 50 and 250. If the SSU viscosity at 100° F. is higher than about 250, the resulting flushing oil is too viscous and has too poor solvent properties to meet the prescribed military specifications.

The specifications prescribed by the military for a flushing oil to be used in reactivation of ships which have been "moth-balled" for extended periods of time are stringent with regard to flash point, moisture removal and removal of rust preservative compounds employed in the "moth-balling" procedure. These specifications which are designated MIL–C–15348a are shown in Table I.

TABLE I

Test:	Specifications
Vis., SUS, 100° F	125–150
210° F	38 min.
Pour °F	Minus 15 max.
Flash, PM, closed	250° F., min.
Rusting action (salt water rust test—48 hrs.)	Must pass
Corroding action	Must pass
Compatibility with 2190T oil	Must pass
[1] Emulsion 130° F	Must pass
Dist. water	
[1] Foam Test, ASTM	
Vol. after 10 min.	
seq. I	
seq. II	
seq. III	Must pass
Removal of rust preventive compound	Must pass
Moisture removability	Must pass
Toxicity	Non-toxic
Neutrality	Neutral
[1] Oxidation test, ASTM	Must pass

[1] The specifications require that a blend of 1 per cent flushing oil and 99 per cent 2190T by volume perform as well as 2190T oil in these tests.

The rust preventive compound removal test is performed as follows: Test specimens which are cold rolled steel plates 5" long, 1" wide and approximately 1/16" thick are sand blasted and then supported through a drilled hole and completely immersed for one minute in rust preventive compound (spec. MIL–C–972, grade 2) after which it is removed and allowed to drain in a dust-free atmosphere at 70 to 80° F. for 24 hours and then aged under the same condition for 30 days. The prepared specimen is suspended vertically by means of a wire and immersed in a beaker containing the flushing cleaning oil held at 150° F. After 5 minutes immersion, the specimen is carefully withdrawn without agitation. If the preservative compound is not completely removed, the cleaning oil will be considered as having failed the test.

The moisture removability test is performed as follows: 40 ml. of cutting oil and 40 ml. of distilled water are placed in a graduated cylinder; a paddle is lowered into the cylinder and the mixture is stirred for five minutes at a speed of 1500 R. P. M. The paddle is removed from the emulsion and the test panel is immersed to the bottom of the cylinder. The panel is removed and allowed to drain for two minutes. The panel is then immersed in another graduated cylinder containing 80 ml. of the flushing oil. The position of the panel is reversed every 5 minutes. If after a 30 minute soaking period a visual examination discloses any trace of emulsion or water on the panel, the flushing oil will be considered to have failed the test.

A flushing oil of superior properties is prepared by incorporating a C_{18} alkenyl succinic acid, di-lauryl acid orthophosphate, 2,6-di-tertiary butyl-4-methyl phenol, tripropylene glycol monomethyl ether and a kerosene concentrate of dimethyl silicone in a naphthene base oil having an SSU viscosity at 100° F. of about 200. The composition of the resulting mixture is shown as follows:

	Weight per cent
Naphthene base oil	92.67
Tripropylene glycol monomethyl ether	7.0
2,6-di-tertiary butyl-4-methyl phenol	0.30
Alkenyl succinic acid	0.015
Di-lauryl orthophosphate	0.0025
Silicone concentrate	0.015

The tests on this composition are shown in Table II:

TABLE II

Vis. SSU, 100° F.	140.5
Vis. SSU, 210° F.	40.2
Pour, °F.	Minus 30
Flash, PM, closed, °F.	275, 275
Rusting action (salt water rust test, 48 hrs.)	Passes
Corroding action	Passes
Compatibility with 2190T oil	Passes
[1] Emulsion 130° F.	13 min.
Dist. water (act. sepn.)	8 cc. cuff
[1] Foam test, ASTM	
Vol. after 10 min.	
seq. I	0
seq. II	0
seq. III	0
Removal of rust preventive compound	Satisfactory
Moisture removability	Satisfactory
Toxicity	———
Neutrality	Neutral
[1] Oxidation test	Equiv. to NS 2190T oil

[1] These tests are run on a blend composed of 1 per cent flushing oil and 99 per cent NS 2190T oil by volume.

The high flash point possessed by the flushing oil of this invention is particularly noteworthy. The flash point of the flushing oil is 25° F. higher than the 250° F. minimum required in the military specification. Presently known flushing oils just meet the minimum flash point requirement so that the flushing oils of this invention have approximately a 25° F. improvement over known compositions. This 25° F. improvement in the flash point substantially reduces the fire hazard involved in the use of these materials and makes them particularly preferred flushing oils for use in reactivation of military equipment.

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 high flash point flushing oil characterized by rustproof, antioxidant and drying properties which comprises a mineral lubricating oil as a major constituent, 0.001 to 2 per cent by weight of an oil-miscible aliphatic dicarboxylic acid having at least 10 carbon atoms, 0.0001 to 1 per cent by weight of an oil-miscible aliphatic acid phosphate containing at least 10 aliphatic carbon atoms, 0.05 to 3.0 per cent by weight of an oil-miscible alkylated phenol and 4 to 10 per cent by weight of tripropylene glycol monomethyl ether.

2. A flushing oil of the type described in claim 1 which contains approximately 0.0005 to 0.01 per cent by weight of an organic hydrocarbon-substituted silicone.

3. A flushing oil of the type described in claim 1 which contains 0.01 to 0.5 per cent by weight of alkenyl succinic acid.

4. A flushing oil of the type described in claim 1 containing 0.1 to 1.5 per cent by weight of 2,6-di-tertiary butyl-4-methyl phenol.

5. A flushing oil of the type described in claim 1 containing 0.001 to 0.03 per cent by weight of aliphatic acid phosphate in which the aliphatic group contains at least 10 carbon atoms.

6. A lubricating composition of the type described in claim 1 in which a naphthene base lubricating oil fraction having an SSU at 100° F. between 50 and 250 is used.

7. A high flash point flushing oil comprising 90 to 95 per cent by weight of naphthene base oil having an SSU at 100° F. of 200, 5 to 8 per cent by weight of tripropylene glycol monomethyl ether, 0.1 to 1.5 per cent by weight of 2,6-di-tertiary butyl-4-methyl phenol, 0.01 to 0.5 per cent by weight of alkenyl succinic acid, 0.001 to 0.03 per cent by weight of dialkyl acid orthophosphate and 0.005 to 0.3 per cent by weight of a kerosene concentrate containing 12 per cent by weight of a hydrocarbon-substituted silicone.

8. A flushing oil of the type described in claim 7 comprising 92.6 per cent by weight of naphthene base oil, 7 per cent by weight of tripropylene glycol monomethyl ether, 0.3 per cent by weight of 2,6-di-tertiary butyl-4-methyl phenol, 0.015 per cent by weight of C_{18} alkenyl succinic acid, 0.0025 per cent by weight of di-lauryl acid orthophosphate and 0.015 per cent by weight of a kerosene concentrate containing 12 per cent by weight of dimethyl silicone.

References Cited in the file of this patent

UNITED STATES PATENTS

1,730,061	Davidson	Oct. 1, 1929
2,442,672	Von Fuchs et al.	June 1, 1948
2,453,319	Patterson et al.	Oct. 26, 1948
2,485,150	Glavis	Oct. 18, 1949