CORROSION PREVENTIVE OILS

Lemuel S. Benbury, Whittier, and Robert F. Connolly, Temple City, Calif., assignors to Bray Chemical Company, Los Angeles, Calif., a corporation of California


6 Claims. (Cl. 252—33.4)

This invention relates to corrosion preventive oils and particularly corrosion preventive mineral lubricating oils and methods of manufacture. More particularly, the invention relates to anti-corrosive oils which meet the requirements of the military specification for humidity protection—MIL-L-644A, and also U. S. Army Specification No. 2-126, AN-VV-C-5756 and MIL-C-7853, for acid corrosion and for salt water immersion. One object of the invention is to produce a lubricating oil which will pass all of the foregoing tests and at the same time will also be satisfactory from the standpoint of color, volatility, flash point, pour point, viscosity, oxidation resistance, and other requirements for high grade lubricating oils. Another object of the invention is to provide a satisfactory oil of this type by combining relatively inexpensive ingredients in amounts which are sufficient small to keep the cost of the product within the range required for the purposes to which anti-corrosion oils are adapted. A further object is to produce a crankcase oil which will pass the requirements of USA 2-1046 and MIL-O-2104 as regards performance in an engine and still pass the corrosion protection and hydrobromic acid neutralization requirements of USA 2-126. In the past it has been common practice to use such quantities of sodium sulfonates in USA 2-126 oils that it interfered with operation of the engine. It has heretofore been the practice to prepare anti-corrosion oils of the type herebefore described by blending hydrocarbon lubricating oils with minor amounts of salts of organic acids commonly known as soaps. For this purpose there have been used soaps of fatty acids, sulfonated fats and sulfonated petroleum hydrocarbons, particularly the preferrentially oil soluble petroleum sulfonates commonly known as "mahogany soaps." In order to pass the acid corrosion test it has previously been the practice to employ the water dispersible soaps, particularly sodium mahogany sulfonate, inasmuch as the highly oil soluble mahogany sulfonates of polyvalent metals, such as calcium and barium, have been ineffective in meeting the requirements of the acid corrosion test No. 2-126, commonly called the "hydrobromic acid test."

The following is a brief description of the tests hereinabove referred to:


Two sandblasted test panels (2x3 inches) are separately totally immersed for not more than one second in aqueous hydrobromic acid of 0.1% concentration and, within one second, in the sample of the oil to be tested maintained at room temperature. The panels are totally immersed in the oil and removed 12 times in 60 seconds. The panels are then stored in a laboratory atmosphere for 4 hours after which the extent of corrosion is observed. To pass the test, no corrosion, staining or other attack shall be evident upon the panels.

B. Salt water immersion test—U. S. Army Specification 2-126, Aug. 6, 1946

Three test panels are separately immersed and swished back and forth for one minute in the oil under test at 77° F. and allowed to drain for 20 hours, suspended. The panels are then separately immersed for 20 hours in synthetic sea water, prepared in accordance with Specification VV-L-791, Method 4011.2, maintained at 77° F., adjusted to a pH value of 7.8 to 8.2. After 20 hours immersion, panels are rinsed in distilled water, acetone and precipitation naphtha, dried and inspected immediately. At least one of the panels shall show no corrosion spots and one panel may show not more than three corrosion spots of not more than 1 mm. in diameter.

C. Humidity test—MIL-L-644A—Feb. 15, 1952

Two steel test panels are immersed in the lubricating oil in question at room temperature for one minute and drained for two hours. The panels are then suspended in a humidity cabinet operated in accordance with Specification JAN-H-792 for 200 hours. At the end of the test no more than a trace of corrosion should be visible on either panel. A trace of corrosion is defined as the presence of not more than three spots of corrosion, no one of which is more than 1 mm. in diameter.

It has heretofore been found that the salt water immersion test can be met by the use of calcium or barium mahogany sulfonate of relatively high molecular weight upwards of about 485, whereas this sulfonate is ineffective in meeting the hydrobromic acid test. Thus a blend of transformer oil 8.4 cs. @ 100° F. was prepared with calcium mahogany sulfonate in quantity sufficient to give an ash value of 0.48%. The resulting oil failed to pass the hydrobromic acid test but successfully passed the salt water immersion and humidity tests. In the case of a sulfonate of lower molecular weight, e. g. 400 molecular weight, prepared from sulfonation of alkylated benzene, a blend of transformer oil with sufficient sulfonate to give an ash of 0.55%, successfully passed the hydrobromic acid test but failed the salt water immersion test, and gave only marginal protection in the humidity cabinet. Various synergistic agents have been added to the alkali earth metal sulfonates in an attempt to provide a product which will successfully pass both the hydrobromic acid test and the salt water immersion test, as well as the humidity test, with only indifferent results. High molecular weight amines such as the fatty amines and aromatic amines, phenol ethers and water dispersable soaps of alkali and alkali earth metals, have given some promise but the amounts required have been excessive and generally the hydrobromic acid protection has been insufficient. In our research, a variety of alcohols, esters, ethers, and glycols were tested, mostly without success in meeting the hydrobromic acid test. For example, a sample of commercial lauryl alcohol failed in concentrations of as high as 1% based on the weight of the compounded lubricating oil. Compounds of glyceryl mono-oleate, decyl alcohol, sodium oleate, various vatering agents and many similar compounds failed to pass the test.

We then discovered that oil soluble glycols of 6 carbon atoms and above are exceptionally effective synergistic agents for the polyvalent metal sulfonates in corrosion preventive oils. Examples are hexylene glycol, octylene glycol, polypropylene glycols and polybutylene glycols. In general, it is desirable that the glycol have a flash point above about 250° F. In order that the compounded anti-corrosion oil will satisfactorily meet flash specifications. We have found that the glycols are incompletely miscible with water are particularly effective, but they should have power to dissolve water, for example
to the extent of about 1 to 20%. We have also found that the glycols having molecular weights upwards of about 500, for example about 1000 to 3000, are still more effective in meeting the HBR corrosion test. The term "glycol" is used in this specification to mean organic compounds having two free hydroxyl groups. They can be on adjacent carbon atoms but the effectiveness of our glycol synergists appears to increase when the hydroxyl groups are further spaced. The presence of other oxygen atoms in the carbon chain also appears to enhance the synergistic effect.

When using water miscible glycols, larger amounts are required, for example, 1% of the final oil blend. Water miscibility also increases the loss of the synergist from the oil film when in contact with water.

The following tests were made on transformer oil containing sufficient calcium mahogany sulfonate of 500 equivalent wt. to provide 0.24% ash and an equivalent amount of the calcium salt of an alkyl benzene sul- fonate of about 400 mol. wt. To this oil was added varying amounts of synergistic agents and the product was subjected to the hydrobromide acid test with the following results:

<table>
<thead>
<tr>
<th>Concentration of Agent</th>
<th>0.0</th>
<th>0.25</th>
<th>0.5</th>
<th>0.75</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexylene glycol</td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
</tr>
<tr>
<td>Oxyethylene glycol</td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
</tr>
<tr>
<td>Polypropylene glycol</td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
</tr>
<tr>
<td>Polyethylene glycol</td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
</tr>
<tr>
<td>2-ethyl-1,3-pentylene</td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
</tr>
<tr>
<td>propanol ether</td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
</tr>
</tbody>
</table>

Another oil was made with transformer oil containing only calcium mahogany sulfonate (500 eq. wt.) sufficient to give 0.24% ash and 0.05% of polypropylene glycol (2025 mol. wt.). This oil successfully passed all three tests, hydrobromide acid, salt water immersion, and humidity.

We have no satisfactory theory for the efficiency of these synergistic coupling agents. Possibly they form with the sulfonate an association compound which can hasten the denaturing action of the polyvalent metal sul- fonates when brought into contact with a metal sur- face which has been wetted with water or acid or which is submerged in water or brine. The free hydroxyl groups may cooperate to associate and remove molecules from the water phase on the metal surface, permitting the oil to wet the metal. The glycols used in our invention possess two hydroxyl groups in the molecule and in the case of the polyglycols there are present also one or more other linkages.

In manufacturing our improved anti-corrosion oils, we prefer to sulfonate a mineral lubricating oil of about 100 to 1000 seconds Saybolt viscosity at 100°F., so that the resulting sulfonate will have a molecular weight of about 450 to 550. Oils from aromatic type crudes are desirable and best results are obtained when the lubricating distildate is preliminarily refined with a moderate acid treatment, e.g. 25 to 100 lbs. acid per bbl. 93–96% H₂SO₃, or the distillate can be initially extracted with a selective solvent such as Chlorex or furfural, thereby removing the most highly aromatic substances believed to contain condensed aromatic rings.

We can also use alkylated aromatic hydrocarbons, for example, those prepared by alkylating benzene with ole- fine polymers such as polypropylene or polybutylene, usually the tetramer or heavier. After sulfonating, the oil is separated from sludge and neutralized with a suitable base, e.g. NaOH, Ba(OH)₂ or lime. If the soda soap is made, it can be purified and concentrated by methods well known, for example, as described in U. S. 2,453,690, U. B. Bray, then converted to calcium, strontium, barium, magnesium or other polyvalent metal sulfonate by metathesis with the corresponding water soluble salt. After excess salt has been washed out in the presence of a suitable emulsion breaker, such as butyl alcohol, the oil can conveniently be dried by heating to about 300 to 400°F., and filtered while hot to give a bright, clear product of a red-brown color, a suitable filter aid, such as diatomaceous earth or carbon being used in the filtration. In the case of alkaline earth metals, the addition of the base to the oil before or dur- ing dehydration gives a basic sulfonate, usually with an alkali value equivalent to about 2 to 20 mg. KOH/gm. Higher alkali values up to 40–60 are also obtainable, particularly when the added base is barium hydroxide. The product usually contains about 30 to 80% of un- sulfonated oil, depending on the stock treated, method of sulfonation and extent of oil rejection in the purifying and concentrating operation.

The synergistic agent can be added to the concentrated polyvalent metal sulfonate, if desired. Concentrated calcium and barium sulfonates are made by dilution and can be added to the treated oil.

Another oil was made as follows: A Stock, containing a basic soap of a polyvalent metal sulfonate, is made and concentrated by means of solvents in the purification stage. Ash values of 5 to 10 and up to 20 with more basic stocks are characteristic of the prod- uct and the sulfonate concentration is readily determined from the ash value, making allowance for the alkali value and knowing the equivalent weight of the sulfonate. Sulfonate concentration can also be determined by titration with cetyl pyridinium bromide.

The synergistic agent can be added to the sulfonate in the final stage of preparation before or after filtering, or it can be added after dilution of the sulfonate with oil in the finished product. We prefer to prepare a concen- trated blending stock containing sulfonate and synergist which can be added to the mineral oil or other com- position as desired. Such a blending stock can conveniently contain the following:

| 0.53 gal. calcium sulfonate, approx. 40% conc. | 29.5 grams polypropylene glycol, 2025 m. wt. | 100.0 grams Paranox 441 (Enjay Company) |
| 0.45 gal. transformer oil, 53–54 S. S. U. at 100°F. |

This stock can be added to the desired lubricating oil in the ratio of about 1 volume to 9 volumes of oil treated, to give a product which meets the corrosion specifications hereinabove described. The Paraxan, polypropylene glycol having the property of an antioxidant to prevent deterioration by aging in storage and use.

We can also add our sulfonate and synergist to greases, waxes, and other preparations requiring rust protective action, such as cutting oils,flushing compounds, coats-ings for machines in storage, fingerprint removers, etc.

One characteristic of the polyglycols when used in our formulation is a tendency to form gels with the sul- fonates, particularly when preparing concentrates. Thus a calcium sulfonate-oil solution containing about 35 to 40% soap (about 8% ash) was mixed with 1% poly- propylene glycol having an average molecular weight of 2025. On cooling the heated mixture, it solidified to a firm gel, which flowed very slowly whereas the sulfonate solution flowed easily. We have found that this gelling tendency can be largely prevented by adding a small amount, for example 0.5%, of a low molecular weight glycol, for example, hexylene or octylene glycol. The gelling may result from a micelle structure formed by association complexes between the high molecular weight glycol and the sulfonate.

The effect of hexylene glycol on the viscosity of hot oil-sulfonate containing polypropylene glycol is shown in the following:
2,730,126

S. U. Furol Viscosity at 210° F., seconds

(1) Calcium sulfonate concentrate—about 60% oil (ash, % alkali value, 19.3)--------- 155.3
(2) Same as (1) + 1% polypropylene glycol, mol. wt. 2025-------------------------- 124.7
(3) Same as (2) + 1% hexylene glycol------------------ 67.2
(4) Same as (2) + 1% polyethylene glycol------------------- 73.7
(5) Same as (1) + 1% polypropylene glycol, mol. wt. 1025-------------------------- 136.2

Concentrates (3) and (4) were both made into rust preventive oils by mixing with transformer oil to give 0.48% ash. Both passed the H8r corrosion test.

Because of the high flash point and low volatility of the high molecular weight glycols above about 500 mol. wt. the oils in which they are employed also have a high flash point and there is little or no danger of the synergist being lost from the oil film on standing even when exposed to elevated temperatures encountered in engine cylinders, on valve stems, etc. Thus our invention makes it possible for the first time to economically provide a crankcase engine oil which couples the requirements of protection against corrosion under operating conditions (Specification MIL-0-2104) with the requirements of corrosion protection in Specification USA 2-126.

The polyglycols which are so eminently effective in synergizing the rust preventive action of oil soluble sulfonates, have a poly-ether structure as follows:

Polypropylene glycol—OH—CH₂—(OCH₃H₂)ₓ—OH
Polyethylene glycol—OH—CH₂—(OCH₂H₂)ₓ—OH

In these formulas, x represents a number in the range of about 2 to 40, preferably about 10 to 40.

The compounded rust preventive oil of our invention will contain about 0.5 to 10%, preferably about 2 to 5%, of polyvalent metal sulfonate in mineral lubricating oil and about .01 to 1.0% of oil soluble glycol synergist, preferably about 0.05 to 0.25% of glycol having a molecular weight above about 1000. The preferred glycols are soluble in water to only a slight extent, usually in the range of 0.1 to 5% at ordinary temperature. Although we prefer to employ the sulfonates of the alkaline earth metals, calcium, barium and strontium, we can also employ sulfonates of other polyvalent metals, such as magnesium, aluminum, zinc, cadmium and iron, or mixtures thereof with alkaline earth metal sulfonates. Other modifications of our invention will occur to one skilled in the art. For example, we may employ polyesters such as dioctyl adipate, sebacate, etc., in place of part or all of the hydrocarbon oil forming the base of our composition and can also substitute various fatty oils for mineral oils for certain uses. Examples are sperm oil, lard oil, rape seed oil, etc.

Having thus described our invention, what we claim is:

1. An anti-corrosive mineral oil composition comprising in major part a hydrocarbon mineral lubricating oil and a minor amount of a polyvalent metal sulfonate of the preferentially oil soluble type and about 0.01 to 1% of a synergistic agent consisting essentially of an oil soluble glycol of the class consisting of polypropylene and polybutylene glycols of about 500 to 3000 molecular weight.

2. The anti-corrosive mineral oil composition of claim 1 wherein the said polyvalent metal sulfonate is an alkaline earth metal sulfonate having a molecular weight upwards of about 400.

3. A corrosion preventive lubricating oil effective in meeting the requirements of the hydrobromic acid test and the salt water immersion test of U. S. Army Specification 2-126 and also the humidity corrosion test of Military specification MIL-L-644A, which comprises a mineral lubricating oil in major part and blended therewith about 0.5 to 10% of a mahogany sulfonate of an alkaline earth metal selected from the class consisting of barium and calcium in combination with about .01 to 1% of an oil soluble derivative of a glycol of the class consisting of polypropylene and polybutylene glycols of about 500 to 3000 molecular weight.

4. The oil of claim 3 wherein the amount of said glycol is employed in about .05 to 0.25 percent.

5. A rust preventive oil comprised of a major amount of a light lubricating oil, about .05 to 10% of a polyvalent metal sulfonate of the preferentially oil soluble type and about 0.01 to 1% of a water displacing synergist comprising an oil soluble glycol of the class consisting of polypropylene and polybutylene glycols of about 500 to 3000 molecular weight.

6. The oil of claim 5 wherein about 0.2 to 1.0% of a glycol of about 6 to 8 carbon atoms is additionally employed to reduce the viscosity of the composition.

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