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LUBRICATING AND CORROSION-PREVENTING COMPOSITION

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This invention relates to the provision of improved lubricating and corrosion-preventing compositions. In particular, it relates to compositions adapted to lubricate and prevent the corrosion of small firearms such as pistols, rifles, automatic or sub-automatic rifles and machine guns, and especially adapted to provide operationally effective lubrication, and corrosion-prevention, at very low temperatures of use, at -50° F. or -70° F. or lower.

For the protection of such firearms, parts thereof, and accessories therefor, during shipment and storage in boxes or containers, it has been conventional either to smear a heavy, normally solid grease-like substance in thick layers over the surfaces of the arms or parts, or actually to imbed the same in a medium of such grease-like substance. The so-treated arms cannot be put to use (that is, fired) without first removing the protective material, because the latter is difficult to deform at relatively normal room temperatures, and very difficult to deform at lower than normal temperatures. Moreover, the conventional protective material does not possess satisfactory lubricating properties. Consequently, before arms are made ready for action all this grease-like material must be removed in its entirety by disassembling and washing various parts in solvent, then reassembling and oiling with a liquid lubricant, which operations necessarily are time-consuming. This grease-like substance is found very difficult to remove after remaining in storage for longer than periods of 8 months, particularly in respect to removing the substance in its entirety from the surfaces by cleansing with solvents such as petroleum solvents. The material now used is known to change physically and chemically at the interface after aging for periods over 8 months. It has been

throughout a wide range of temperatures including temperatures as low as -70° F. and which simultaneously are effective corrosion-preventives for such firearms (and mechanisms) during shipment and storage. Another inventive object is the provision of liquid preservative lubricant compositions of low viscosity over wide ranges of temperatures, which compositions shall be effective as corrosion-preventives when spread in extremely thin, oily films (by dipping, brushing or spraying) over the surfaces of the firearm parts or of the assembled firearms, which protective films need not be removed when the firearms are put in operation but rather constitute improved lubricating films effective for lubricating the firearms of all temperatures down to as low as -70° F. or lower.

The above, and other, inventive objects are realized by the use of the hereinafter described normally liquid lubricating and corrosion-preventing compositions. They have been found to give satisfactory lubrication and protection against corrosion during shipment, storage and operation of all types of small arms, and especially satisfactory lubrication during the operation of machine guns when fired at temperatures as low as -70° F. The compositions are liquids of low viscosities over wide ranges of temperatures, and provide adequate protection against corrosion of firearms and replacement parts during shipment and storage by spreading an extremely thin coating thereof by dipping, spraying or brushing the parts or assembled firearms. It is unnecessary to remove these new preservative lubricant compositions when the arms are put in operation.

Preferred specific preservative lubricant compositions in accordance with the present invention have properties and characteristics falling within the following ranges:

Flash point, $^{\circ}$ F., minimum	275° (by open cup method)
Pour point, $^{\circ}$ F., maximum	-50° to -70° (by ASTM method)
Viscosity, kinematic:	
Centistokes at 100° F.	12.0 to 20.0
Centistokes at -30° F.	2000 to 6000
Corrosion on copper, brass, bronze, aluminum, magnesium, steel, etc.	Nil
Protection against corrosion	Protect sand-blasted steel (SAE 1020) against corrosion for 200 to 300 hours when tested in a humidity cabinet maintained at 100° F., and 95 to 100% relative humidity.
Immersion corrosion	Protect sand-blasted steel (SAE 1020) against corrosion when immersed in 3½% NaCl solution for 20 hours at room temperature.

found that objectionable, difficultly-soluble substances are formed which are extremely difficult to remove by ordinary means. This substance resembles a gum-like material and is found to be slightly soluble in alcohols or acetone.

It is an object of the present invention to provide normally liquid preservative lubricant compositions, by which expression are here meant normally liquid compositions which are effective lubricants for firearms (and other mechanisms)

In addition to having the above properties, they permit, when used as lubricants for a .50 caliber M-2 basic aircraft machine gun maintained at from -50° F. to -70° F., the automatic firing of 25 line rounds with one round in the gun chamber without stoppage of the gun's operation. These compositions remain brilliantly clear when gradually cooled from room temperature to their solidification points, which desirable property indicates that no objectionable crystalline bodies,

which might interfere with or retard the firing action of a gun, will form therein during severe reduction in temperature.

The liquid preservative lubricant compositions of the present invention are, in general, solutions, in selected light oils (hereinafter more specifically described) of small amounts of alkaline earth metal (preferably calcium) soaps of "Alox acids," of lower alkyl esters of "Alox acids," and of selected anti-oxidants.

By "Alox acids" are here meant the relatively high molecular weight, generally saturated, carboxylic acids derived from petroleum or similar mineral hydrocarbon mixtures by the Burwell process of liquid-phase, controlled, partial oxidation thereof (see U. S. Patents Nos. 1,690,768 and 1,690,769). These "Alox acids" which are here used for preparing the alkaline earth metal soaps and lower alkyl esters are derived from the oxidation of petroleum fractions of lubricating oil grade, preferably derived from the oxidation of well refined lubricating oil stocks which are substantially free from crystalline bodies, and, desirably, also substantially free from asphalts and unsaturated hydrocarbons. Highly refined, propane-extracted paraffine-base oils have been found to be especially suitable. Operable starting materials may range in specific gravity from 29 to 34, in viscosity (at 210° F.) from 40 to 60, and in viscosity index from 80 to 120. Typical is a lubricating oil having a specific gravity of 32.0, a viscosity of 49.6, a viscosity index of 104, and 440° F. flash point.

Addition of such calcium soaps of "Alox acids" to lubricating oils definitely depresses the pour point of the oils. For example, when from 3.5 to 4.5% of the calcium soaps is added to an oil or mixture of oils of different viscosities showing the following pours, the pour point is further depressed, as shown:

Oil A, pour point -40° F.----Depressed to -60° F.
Oil B, pour point -45° F.----Depressed to -65° F.
Oil C, pour point -55° F.----Depressed to -70° F.
Oil D, pour point -65° F.----Depressed to -80° F.,
and lower.

Also, the calcium soaps of Alox acids exert a definite—and desirable—corrosion-preventing action in the composition.

The degree of protection which the new preservative lubricant composition provides steel surfaces under atmospheric exposure (moist air) is related to the amount of calcium (or other alkaline earth metal) soaps of "Alox acids" present in said composition. Preferably, the calcium soap is present in the composition in an amount from 1% to 4.5%, preferably from 3.0% to 4.5%, by weight. Illustrative of the variation are the following corrosion data: Panels of SAE 1020 ("low carbon") steel were coated with the coating compounds recited in the table below, and were exposed in a cabinet in which the atmosphere, kept moving, was maintained at 95-100% relative humidity and at a temperature of 100° F., corroded at the rates shown:

	Coating compound	No. of hours before corrosion appeared
1	Light transformer oil of low pour point, viscosity 9.5 centistokes at 100° F.	
2	Same oil+1.0% Ca soaps.....	Between 1 and 2 hours.
3	Same oil+2.0% Ca soaps.....	Between 5 and 7 hours.
4	Same oil+3.0% Ca soaps.....	Between 24 and 36 hours.
5	Same oil+3.5% Ca soaps.....	Between 150 and 200 hours.
6	Same oil+4.5% Ca soaps.....	Between 200 and 300 hours.
		Between 450 and 600 hours.

The preservative action toward steel of an oil solution of the aforesaid calcium soaps is considerably weaker in the immersion test than in the moist air test. Thus, in the case of composition #5 of the above table, the coated steel panel showed corrosion after being immersed in tap water for 48 hours, and corroded in a shorter time of immersion in a 3.5% solution of NaCl in water. However, it has been found that the addition of from 0.5% to 1.0% (by weight) of methyl esters of "Alox acids" to composition #5 gives a moist air test of 150-200 hours, a tap water test of longer than 100 hours, and a 3.5% of NaCl solution test of from 75 to 100 hours. Similar improvement as to immersion test results follows generally from addition of these (or similar low molecular weight) alkyl esters of Alox acids to lubricating oil solutions of calcium soaps of Alox acid. Instead of the methyl esters there may be used the corresponding ethyl, propyl or butyl esters of the Alox acids. The Alox acids employed in forming the alkyl esters may be those derived from partially oxidized mineral lubricating oils of the types hereinbefore described.

The anti-oxidants which are used in preparing the compositions of the present invention are thio-ethers and include: thio-ethers of higher alkyl phenols such as amyl phenol and octyl phenol, and thio-ethers of mon-atomic aliphatic alcohols having six or more atoms in the chain (straight, or branched). Preferably, the thio-ether of tertiary amyl phenol is employed, in an amount of the order of 0.5-1.0% by weight. These thio-ethers are effective in the composition to prevent excessive oxidation of the latter when the same is subjected to relatively high temperature, particularly, in rapid-firing guns such as machine guns and sub-automatic machine guns: also, they are beneficial in holding in solution slight amounts of hydroxy hydrocarbon soaps which may appear in the alkaline earth metal soaps of the "Alox acids."

The light oil which is used as the diluent or "solvent" component of the present compositions is a highly refined petroleum lubricating oil of low pour test, e. g., a highly refined transformer oil. Preferably, there is used an oil which has the following properties and characteristics:

Flash point, minimum.....	300° F.
Pour point.....	-50° to -65° F.
Viscosity at 100° F. centistokes...	9.5-10.0
Viscosity at -30° F. do.....	1500-2000
Engler distillation range:	
Initial boiling point.....	250-280° cent.
10%.....	308-310° cent.
50%.....	330-350° cent.
Oxidation by Norma Hoffman	
bomb method.....	400 hours, not to exceed 25% drop of initial pressure
Gum deposition.....	Nil
Color after 400 hours' exposure..	Not lower than #6 N. P. A.
Water content.....	Nil

In this connection it is noted that oils—of the same viscosity and distillation range—from different sources show a wide variation as to rate of evaporation from metal surfaces. Thus, an oil from California crude evaporates from a metal surface much faster than does an oil (of the same viscosity and distillation range) from Pennsylvania crude, and an oil from Venezuelan crude evaporates somewhat more slowly than

does the oil from Pennsylvania crude. Because of these facts, it is preferred to employ, as the diluent or "solvent" component of the present compositions, oils refined from Venezuelan or Pennsylvania crudes.

For preparing the calcium soaps component of the compositions of the present invention the procedure may be as follows: The starting material (that is, the oil) is oxidized, by the Burwell process, for a period of from 4 to 6 hours or until the reaction mass has acquired an acid number of from 12 to 17. The partially oxidized mass is washed with water to remove any water-soluble components. The washed mass is then treated with aqueous caustic alkali to saponify the saponifiable components thereof, and the resulting mixture is thereafter maintained for some time in a quiescent state in order to permit substantially complete separation between the resulting soaps and the unsaponifiable components of the mass. After such separation, the soaps-containing layer is removed from the settling chamber and the alkali metal (e. g., sodium) soaps are recovered and converted to calcium soaps by reaction with calcium chloride. The calcium soaps are washed free from chlorides, and are blended with oil for further treatment and filtration. The oil selected for the blending step preferably is the same as that subsequently to be used in extending the eventual concentrate to the final preservative lubricant composition.

Complete conversion of the alkali metal soaps of the Alox acids to calcium soaps is not effected by the double decomposition method with calcium chloride, and hence it is necessary or at least advisable to complete the conversion to calcium soaps by "liming" the product: This step is effected by treating the material, at relatively high temperature (i. e., at above 100° C.) with an excess of calcium hydroxide. Water is driven off by heating the limed material to a top temperature of say 160° C. The liming treatment not only converts residual sodium soaps to calcium soaps but also neutralizes any acids which may have been occluded in the soap mixture. The liming treatment may be practiced immediately after the double decomposition with calcium chloride, but preferably is practiced after the product of the double decomposition step has been blended with sufficient oil to make the "concentrate" hereinafter described.

After the liming, the limed material is maintained in quiescent state for several hours to permit the settling out of excess lime, and is then filtered.

The filtered limed blend of calcium soaps in oil is then combined with the lower alkyl esters component and with the thio-ether component, whereby to complete the preparation of a concentrate which may be suitably extended with a further portion of the aforesaid diluent oil, or with a mixture of diluent oils, to provide the final preservative lubricant composition. The con-

centrate, according to a preferred embodiment of the invention, consists of

Parts by weight

5	A 25 to 35% solution of the aforesaid calcium soaps of Alox acids in a highly refined transformer oil of low pour point, preferably -50° F. or lower.....	10-15
10	Thio-ether of tertiary amyl phenol (or equivalent oxidation-depressing thio-ether compound)	0.5-1.0
	The aforesaid methyl (or other lower alkyl) esters of Alox acids.....	0.5-1.0

To convert this concentrate to the final preservative lubricant composition the same is extended with sufficient "diluent" oil to make the total 100 parts by weight. The diluent oil may consist of a highly refined oil having the properties hereinbefore set out, e. g., a transformer oil of low pour point; preferably -50° F. or lower, or (as where a less extremely low temperature product is indicated) it may consist of a major amount of the latter with a minor amount (say, 10 to 15 parts by weight) of another oil such, for instance, as a Mid-Continent oil having a pour point between 0° and -10° F. and a viscosity of 180-250 S. U. V. at 100° F.

We claim:

1. A preservative lubricant composition substantially consisting of a highly refined hydrocarbon oil derived from Venezuelan or Pennsylvanian crude oil and having a pour point at least as low as -40° F. containing dissolved therein from about 3.0% to about 4.5% by weight of calcium soaps of acids derived from the oxidation of a petroleum lubricating oil substantially free from crystalline bodies, asphalts and unsaturated hydrocarbons, and from about 0.5% to about 1.0% by weight of lower alkyl esters of said acids, the resulting solution also containing a small amount of an oxidation-depressing thio-ether of an alcohol, said preservative lubricant composition having a pour point at least 20° F. below that of the hydrocarbon oil component of the composition.
2. A preservative lubricant composition substantially consisting of a highly refined hydrocarbon oil having a pour point not higher than about -40° F. containing dissolved therein calcium soaps and methyl esters of acids derived from the oxidation of petroleum lubricating oils substantially free from crystalline bodies, asphalts and unsaturated hydrocarbons, the calcium soaps of said acids being present in an amount of from about 3.5% to about 4.5% by weight and the methyl esters of said acids being present in an amount of from about 0.5% to about 1.0%, and a relatively very small amount of an oil-soluble oxidation-depressing thio-ether, said composition having a pour test at least 20° F. below that of the hydrocarbon oil component of the composition.

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