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LUBRICATING COMPOSITION

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This invention relates to lubricating compositions adapted for use under high temperature and oxidation conditions. This application is a continuation-in-part of my copending application, Serial No. 466,945 filed November 25, 1942.

In order to provide more satisfactory lubrication of the engine parts lubricated by crankcase oil, it has been deemed necessary to highly refine mineral oil lubricants. The more highly refined lubricant, such as is obtained by solvent treating, has a high viscosity index and reduced tendency to form sludges and colored bodies which deposit out on the surfaces contacted by the oil. It has been found, however, that these highly refined lubricants are subject to oxidation which causes the formation of oxygenated bodies, metallic contaminants, and organic acids which coact to corrode the more sensitive bearing metals now commonly used in the crankcase. Furthermore, even though the highly refined mineral oil is resistant to sludge formation, it has a tendency to form lacquerous formations upon the piston rings, cylinder walls, pistons, and other parts of the engine that become heated in use. Lacquer deposits cause sticking of the piston rings and eventual failure of the engine, thus necessitating replacement of the engine parts, which is a costly process both in respect to the cost of material and in delay.

The less highly refined mineral oils are less prone to form corrosive products by oxidation or deterioration but are more inclined to form sludges and darkened products. However, even the less highly refined oils form corrosive products after prolonged use.

In order to prevent or counteract the destructive tendencies of the readily oxidized mineral oils, various addition agents for preventing oil deterioration have been incorporated into these oils. These addition agents may be roughly classified into two types; one type may be called "antioxidants" because the compounds within this group tend to prevent or reduce the oxidation and deterioration of the mineral oil; the other type may be called "precipitants" or "inhibitors" because the compounds so designated react with and precipitate out or otherwise pacify corrosion and oxidation accelerators in the oil. By means of these addition agents, oxidation of the lubricant and corrosion are retarded or stopped. In general, phosphorus compounds are classifiable as "antioxidants" whereas sulfur compounds are classifiable as "precipitants" or "inhibitors."

The lacquer forming tendencies of the lubricants may be reduced by certain compounds commonly called "detergents." These compounds are generally metal containing organic compounds in the form of soaps, salts, or metallo-organic compounds. The oil containing these materials washes, laves, flushes, or colloiddally removes the

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lacquerous deposits from the various engine parts, thus leaving the metal clean and bright. Diesel engines, for example, must use crank case oils that are exceptionally nonlacquer forming: the oil must contain a "detergent" type addition agent to provide effective and efficient lubrication.

There is another type of addition agent which is closely related to the "detergent" additive mentioned above. This type may be called the "peptizers" because they have the capability of maintaining sludge, sludge-like materials, and other insoluble colored bodies in suspension in the lubricant rather than permitting them to deposit upon the surfaces of the bearing and other metallic parts of the engine. The materials are kept in a colloidal or dispersed state in the lubricant, thus preventing plugging of oil lines, gumming of the valves, and freezing of the piston rings. An addition agent or combination of addition agents having the quality of detergency and peptizing power are necessary additives for heavy-duty engines, such as Diesel, aviation, and marine engines, to suspend soot present in the oil from incomplete fuel combustion.

Various chlorine and sulfur compounds have been added to lubricants which are to be used under "extreme" and "mild extreme" pressure conditions. The improvement thus effected in a lubricating oil has been made desirable and even necessary because of the increased bearing pressures per unit area, the smaller bearing clearances and the higher speeds and temperatures now almost universally used in the modern machinery.

Another useful property of a lubricant is "oiliness," which may be defined as that property of a lubricant that causes it to give a lower coefficient of friction (generally at slow speeds or high loads) than another fluid of the same viscosity. This property of a lubricant is of great importance under thin film lubrication or nonviscous lubrication conditions such as are found when idle machines are being started or in cold weather conditions, during which the fluid lubricant is not flooded over the rubbing surfaces.

To my knowledge none of the metal tetrathio-phosphates have been added to lubrication compositions of the prior art. I have found that the addition of these compounds or mixtures of these compounds improves the film strength, the oxidation resistance, the noncorrosiveness, the detergency, the peptizing power, and other desirable characteristics of a lubricant to an exceptional degree.

An object of this invention is to provide improved lubricants for crankcase and other lubrication.

A further object of this invention is to provide a lubricant having improved film strength, re-

stance to oxidation, detergency, capability to maintain sludges and insoluble matter in suspension, and noncorrosive action on bearing metal.

Other advantages and objects of my invention will become apparent in the course of the following description.

My invention comprises the addition of small but effective proportions of certain inorganic metal tetrathiophosphates to lubricating compositions. Very small proportions ranging from 0.001 to 5.0 per cent may be added to a lubricant to improve the various desirable characteristics of the lubricant. Very small amounts are extremely effective and only under unusual circumstances is it necessary to add an amount of the additive in excess of 0.05 per cent by weight to the lubricant. The compounds within the scope of this invention have the formula, MPS_4 , $MM'PS_4$, or $MM'M''PS_4$. M, M' M'' represent ammonium and the metal elements. Barium, potassium, sodium, calcium, tin, lead, aluminum, zinc, lithium, strontium, and other metals can be employed. The ammonium radical may also be employed.

The choice of metal depends in part upon the particular type of oil to which the metal tetrathiophosphate is to be added and the particular use for which the lubricant is to be employed. If the lubricant is designed for use in a Diesel engine, or a heavy-duty engine having a powerful tendency toward the formation of sludges and lacquers and wherein large amounts of extraneous contaminants such as soot gain access to the oil, the alkaline earth metal tetrathiophosphate compounds are preferred, as these exhibit greater detergency than do the other compounds; however all of the compounds are more or less potent detergents and are therefore effective additives for lubricants to be used under severe conditions. The tin and tetravalent lead tetrathiophosphates are better antioxidants than are the other compounds and are therefore of great value when it is desired to prepare an oil for use under severe oxidation conditions.

The metal tetrathiophosphates are prepared by mixing the correct amounts of P_2S_5 and the sulfide of the desired metal or metals and elevating the temperature. This reaction may be induced either with or without the use of solvents. A highly effective solvent for this purpose is molten sulfur. The temperature required to induce the reaction depends on the metal sulfide used and varies from 60° F. for the low molecular weight alkaline earth metals to as much as 600° F. for the higher molecular weight metals. Those metal sulfides requiring more than 100° F. to start the reaction are reacted in the presence of an inert gas such as nitrogen to prevent oxidation.

An effective method for preparing metal tetrathiophosphates comprises fusing a mixture of sulfur, phosphorus pentasulfide, and the sulfide of the desired metal. The phosphorus pentasulfide and metal sulfide should be in the proportion calculated to produce the desired metal tetrathiophosphate and the sulfur may vary from five to ninety per cent of the total mixture. The metal tetrathiophosphate may then be recovered from the fused mass by fractional crystallization from carbon disulfide or other suitable solvent.

A convenient method, using a solvent, comprises adding to the lubricating oil base stock a mixture of P_2S_5 and the metallic sulfide in the proportion necessary to produce the desired per-

centage of metal tetrathiophosphate, just prior to the blending operation for producing the desired grade.

It is to be understood that my invention is not limited to these particular methods of making the compositions and they are only given to clarify the invention.

The metal tetrathiophosphates may be added to the lubricating composition by dissolving or suspending, or otherwise mixing the compounds in the oil, or the compounds may be added to the oil and the resultant composition heated to effect a reaction to further modify the lubricating composition. The oil containing a small proportion of the metal tetrathiophosphate may be heated from between 150° F. to 350° F. for a period of time which may vary between a few minutes to about four hours or longer. A lubricating composition quite stable toward the formation of lacquers and gums may be made by heating the oil blended with a small proportion of the additive while air is blown through the composition. In the preparation of several lubricating compositions, the oil and metal tetrathiophosphate was heated to 150° F. for three hours then further heated to 350° F. for 20 minutes. The lubricant thus formed proved to be different from the compositions which had not been heated. The heated product was found to be less corrosive to copper strip when tested by heating the oil for long periods of time at very high temperatures. This knowledge helps to explain the action of the additives on the lubricant in service.

Under the severe surface conditions of elevated temperatures the inorganic metal tetrathiophosphates are quite stable when compared to the organic metal tetrathiophosphates which decompose more readily under elevated temperatures.

Such stability retards the rate of reaction and broadens the time limits of effectiveness on the inorganic compounds. These inorganic compounds are alkaline whereas the organic compounds are neutral or slightly acidic.

The metal tetrathiophosphates may also be added to the oil while in use in an engine by placing a suitable container filled with the metal tetrathiophosphates in the oil circulating system so the oil circulates through this material. A conventional oil filter cartridge may be used for this purpose.

The addition agents and the lubricants of this invention have the precipitating characteristics of lubricants containing certain sulfur compounds; that is, they slowly release or otherwise provide sulfur in the oil which reacts with the catalytically active metallic contaminants such as lead oxide and iron oxide and the lead and iron organic compounds present in the oil to render them catalytically inactive; thus rendering the lubricant safely operable for longer periods of time, even under severe conditions.

These compounds also impart antioxidant characteristics to the oil into which they are incorporated. This effect is thought to be due to the presence of phosphorus in the compounds. In comparison with organic sulfur-containing addition agents which show an accelerating action on the oxidation and deterioration of oils when tested in glass equipment such as the Indiana oxidation apparatus, the inorganic metal sulfur phosphorus compounds of my invention lengthen the induction period necessary to initiate the oxidation of the oil in such apparatus. The belief is that the organic compounds commonly used as sulfur carriers for the sulfur-bearing ad-

dition agents of the prior art are themselves more prone to oxidize than is the oil base to which they are added. When tested in glass equipment, they, the organic compounds, decompose, forming sludges and oxidation products, whereas the compounds of this invention, being inorganic compounds, do not decompose or react with oxygen to form sludge-like bodies in the oil.

The metal tetrathiophosphates, $M_2(PS_4)_3$, may be dissolved, dispersed, or otherwise incorporated in the lubricating oil. The solubility of some of the various metal tetrathiophosphates in oil is quite low but the low solubility is sufficient in nearly all cases. The solubility of the various metal tetrathiophosphates varies with the particular type of lubricating oil and the particular fraction of the lubricating oil. It is thus possible to select some base oils which may be more heavily fortified by higher concentrations of the addition agent.

A useful modification of this invention is the utilization of solubilizing agents such as esters of thiophosphoric acid to increase the solubility of metal thiophosphates in the oil.

Modified Underwood oxidation and corrosion tests on blends of highly solvent-treated lubricants containing as improving agents these metal tetrathiophosphates proved that the lubricating composition of this invention requires a much longer period of time before corrosion of cadmium-silver and copper lead bearings takes place. Naphtha and chloroform insolubles were only minutely present, although the insoluble constituents of the straight (unblended) mineral oil were present in very high proportions after a brief period of time in the Underwood machine.

It is sometimes advantageous to include other addition agents in the lubricating composition. Addends for specific purposes may be incorporated into my lubricant. Such addends may be a pour point depressor such as a naphthalenechlor wax condensation product, a viscosity index improver such as certain resins or polymerized hydrocarbons; metal soaps and other thickening agents such as fibre, hair, mica, and graphite.

Chlorine bearing compounds may be added to improve the film strength of the lubricant and otherwise to improve the lubricating composition; and this is a useful adjunct to my invention. Calcium dichlorostearate, chlorinated paraffin wax, chlorinated octadecanol, dichloropropyl ether, chlorobutyron, octadecyl trichloroacetate, methyl dichlorostearate, chlorotolyl stearamide, chloro-oleyl amine, chloro-oleyl amide, barium derivative of tertiary amyl phenyl sulfide, pentachlorodiphenyl, a chlorinated wax-naphthalene condensation product containing residual chlorine, trichlorophenol, trichlorodiphenyl ether, chlorodiphenylene oxide, chlorophenyl stearic acid, o-chloro-acetophenone, chlorobenzophenone, pentochloro-phenylbenzoate, chlorobenzanilide, chlorophenyl phosphate, chlorophenyl phosphite, chlorophenyl, and similar halogen bearing compounds enhance the action of the addition agents on the lubricating oil.

Furthermore, I have found that various other addition agents, such as are hereinabove designated as oil deterioration preventing addition agents, may be added to the lubricating composition to improve the lubricating and stability characteristics of the lubricating blend.

Sulfur compounds may be utilized in combina-

tion with the metal thiophosphates and lubricating oil to augment the lubricating compositions to oxidation and thus render the oil less corrosive to sensitive bearing metals over a longer period of time. Some of the sulfurized products which may be incorporated into the oil are: sulfurized high molecular weight unsaturated alcohols, sulfurized esters of unsaturated naturally occurring vegetable and animal oils such as castor oil, corn oil, rapeseed oil, soy bean oil, cotton seed oil, sperm oil, lard oil, etc. Sulfurized olefins obtained from petroleum or petroleum products by fractionation, cracking, halogenation and dehydrohalogenation, or other means, may be employed. In general, any sulfurized hydrocarbon derivative of sufficient stability may be used to impart added qualities to the oil. If the oil is to be used where no readily corroded metal is present, the more unstable types of compounds may be used. If the oil is to be used in the crankcase of internal combustion engines, more care must be used in the selection, as only the more stable sulfur compounds may be safely used.

The inorganic metal tetrathiophosphates are admirably adapted for use in oil of lubricating viscosity of all types including those designated for use in automotive crankcases, Diesel oils, hydrogenated, polymerized, and otherwise synthetically treated oils such as voltolized oils, aluminum chloride treated oils, and the like. Furthermore, the lubricating oil may contain in whole or in part shale oil, animal or vegetable oil, and other oils of lubricating viscosity.

It will be seen that I have accomplished the objects of my invention, namely, to provide an improved lubricating composition having a multifunctional addition agent which vastly improves the performance of the lubricant.

Having thus described my invention, I claim:

1. A lubricant comprising an oil of lubricating viscosity normally tending to oxidize in use having incorporated therein an inorganic tetrathiophosphate in an amount sufficient to inhibit oxidation of the oil.
2. A lubricant comprising in combination a major proportion of an oil of lubricating viscosity and from 0.001 to 1.0 per cent of an inorganic metal tetrathiophosphate.
3. A lubricant comprising in combination a major proportion of an oil of lubricating viscosity and from 0.001 to 1.0 per cent of an inorganic calcium tetrathiophosphate.
4. A lubricant comprising in combination a major proportion of oil of lubricating viscosity and from 0.001 to 1.0 per cent of an inorganic barium tetrathiophosphate.
5. A lubricant comprising in combination a major proportion of oil of lubricating viscosity and from 0.001 to 1.0 per cent of an inorganic tin tetrathiophosphate.

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