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LUBRICATING OIL

Bert H. Lincoln and Gordon D. Byrkit, Ponca City, Okla., assignors, by mesne assignments, to The Lubri-Zol Development Corporation, Cleveland, Ohio, a corporation of Delaware

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Our invention relates to lubricating oils and more particularly to improved lubricating oils of high film strength, high resistance, to oxidation, and markedly reduced formation of corrosive products during use.

Present-day mechanical devices require lubricating oils of high film strength, of high oiliness characteristics, and of low tendency to oxidize during use. It has been found that the present-day hydrocarbon lubricants of the very highest quality are deficient in these very important characteristics. These three properties are of vital importance under conditions of thin film lubrication where the lubricant has been squeezed from between the friction surfaces because of high pressure, slow speeds, and other causes. In modern engines, large surfaces of oil are exposed to the action of atmospheric oxygen, promoting rapid oxidation. It is readily seen that the viscosity or the body of the lubricant plays no part in thin film lubrication and that the remaining film of oil must have a very high film strength and be of high oiliness value to prevent rupture of the film of the lubricant, which would cause seizure. The oil film must tend to keep the coefficient of friction as low as possible. The oil must resist oxidation when these thin films are heated in the presence of atmospheric oxygen as they are in use.

Mechanical devices are being designed for higher pressure operation, and the film strength of the best quality straight hydrocarbon lubricant has been found to be too low for satisfactory service. It will be obvious that an invention which provides a means of improving the film strength of these lubricants is of great importance to the art of lubricant manufacture and to the designer and fabricator of mechanical devices.

Substantially all machines operate in part or at times totally under conditions of boundary or thin film lubrication, under which conditions the oiliness or unctuosity of the lubricant is the first and primary requisite of efficient operation. Those skilled in the art of lubricant manufacture or machine manufacture will readily appreciate the value of an invention that will improve the oiliness of these otherwise high-quality lubricants. Furthermore, sludge and acid are especially deleterious under conditions of thin film lubrication. The sludge is not a lubricant in any sense of the word, and the soluble acid is particularly corrosive to bearing metals such as cadmium-silver, copper-lead, and the like.

In starting idle mechanical equipment which is lubricated from a sump by pumping or circulating the lubricant, there is always a short period of time in which the rubbing surfaces must operate under conditions of dry friction if ordinary hydrocarbon lubricants are used. With dry friction, the wear on friction surfaces is extreme; and during cold weather when the lubricant is sluggish or during periods when the lubricating system is not functioning properly for one reason or another, rubbing surfaces may not only suffer considerable wear but may be damaged to the point where they must be replaced. The product of our invention has a very important property of reacting with the metal surfaces, penetrating or adsorbing on the metal surfaces, and leaving a film of lubricant with high oiliness character, which remains on the metal surface irrespective of the length of time the machine has been idle.

This high oiliness film gives very even and smooth operation, which may be easily discerned by the experienced operator or lubricating engineer.

When the hydrocarbon lubricants are diluted with unburned fuel or with other light hydrocarbons, the small degree of oiliness of the original hydrocarbon lubricant is greatly decreased. We have found that the addition of the products of our invention to hydrocarbon lubricants more than compensates for the loss in oiliness and load-carrying ability from dilution.

It is well known that, in order to obtain lubricants which are preeminently satisfactory from the standpoint of oxidation in use, it is necessary to refine the oil thoroughly and then to add an inhibitor of oxidation. The thorough refining may consist of more and heavier acid treatments or solvent treating so as to remove a considerable part of the oil and leave only the most stable portion. Such drastic refining is necessary in order to obtain stability with respect to sludge formation, but the oil is then subject to easy oxidation to form soluble acids and other corrosive materials. This can be prevented by the addition to the refined oil of small amounts of materials which either prevent the formation of these corrosive products or by some action render them inert. Furthermore, such well-refined oils are susceptible to the formation during use of lacquer-like materials which tend to stick rings. This results in blow-by and hence loss of power, failure of lubrication, scratching, scoring, overheating, and eventually replacement of parts. It is practically impossible to refine a lubricant in such a manner as to avoid all three of these difficulties, namely, sludge, soluble corrosive products, and lacquer. It is considerably more advantageous to add the materials of our invention and avoid these difficulties by this method.

Certain compounds are adsorbed or absorbed by metals forming tenacious films at the surface of metals which are able to stand high pressures. X-ray diffraction methods have shown that compounds containing highly polar molecules, that is, molecules of unsymmetrical electrical charac-

ter containing an atom or group of atoms exhibiting a secondary or residual valence, tend to produce regimentation of the molecules of hydrocarbon oil when added thereto. A metal immersed in a strongly polar compound will show a film of the compound in which there is a regimentation of molecules oriented with respect to the surface of the metal by which they are adsorbed or absorbed.

Many of our additive materials are effective when added to poorly refined or even wholly unrefined lubricants. The addends may thus be substituted in whole or in part for the usual refining processes.

In the prior art of applying these principles to the manufacture of lubricants, many diverse types of materials have been suggested to be added to obtain improvement in various characteristics. It has been found that the addition of various compounds frequently improves film strength, oxidation resistance, noncorrosiveness, and other characteristics.

One object of our invention is to provide improved inhibitors of oxidation and corrosion for addition to lubricants.

Another object of our invention is to provide film strength improving addition agents suitable for use in lubricants and especially in crankcase lubricants.

Other and further objects of our invention will appear in the course of the following description.

In general, our invention contemplates an oil of lubricating viscosity having added thereto a small amount of a metal derivative of an enol. We have found the enols of heavy metals to be more suited to our purpose than the lighter metal enols. By heavy metal, we mean one having an atomic weight of fifty or more. Chromium, copper, zinc, tin, and zirconium are examples. By enol, we mean any organic compound which can exist in keto and enol forms and in which equilibrium mixture sufficient enol exists to permit of the formation of these heavy metal derivatives; beta-diketones are examples. By keto and enol forms in the appended claims, we intend to include the nitrogen analogues, that is, the corresponding lactam and lactim forms as exemplified by the forms of isatin.

The compound may contain additional elements or combinations of elements including the halogens, phosphorus, sulfur, nitrogen, or oxygen.

The metal enols of this invention have a dual action in a lubricant. One action involves increased load-carrying ability and/or oiliness, while another action is directed to the stability of the lubricant. For load-carrying capacity, quantities ranging from 0.1 per cent to about 10 per cent may be added. As an anticorrosive agent and/or an antisludging agent, much smaller amounts may be required ranging from approximately 0.001 or slightly less to 1.0 per cent or slightly more. The action of the metal enols is specific but difficult to understand. These compounds may be added to any type of hydrocarbon lubricants but show an unusual value in highly refined and solvent treated lubricants. By oil having lubricating viscosity in the appended claims, we mean to include the so-called mineral oils and various hydrogenated, polymerized and otherwise synthetically treated oils such as voltolized oils, aluminum chloride treated oils, and the like. Furthermore, the lubricating oil may consist in whole or in part of shale oil, animal or vegetable oils such as castor oil, lard oil, corn oil, cottonseed oil, and the like.

In practice, it is better to employ compounds whose boiling point is above 225 degrees F. in order that the addition compound will not be evaporated or distilled in use. The selection of a particular compound or compounds to be used as an addition agent to the hydrocarbon or other oil is to be made considering the physical and chemical properties of the various compounds and the use to which the blend is put. Thus, if water is likely to be present during use, a metal enol or combination thereof is selected which is not affected by water. If a particular added compound proves too volatile for its application, a higher boiling material should be used and the more volatile compound used for blending in an oil intended for duty at lower temperatures. In general, for automotive crankcase lubricants, we prefer to use compounds having vapor pressures of less than atmospheric at 250 degrees F.

The following compounds may be used in accordance with our invention. All and each of these are to be considered as examples of our invention when blended in an oil of lubricating viscosity:

Copper acetylacetone, stannous acetylacetone, stannic bisacetylacetone dichloride, stannic bisbenzoylacetone dichloride, stannic bisbenzoylacetophenone dichloride, stannic bisacetylacetone dibromide, stannic bisbenzoylacetone dibromide, stannic bisbenzoylacetone dichloride, stannic bisbenzoylmethane dibromide, stannic bis-3-ethylacetylacetone dibromide, chromium propionylacetone, chromium benzoylacetone, chromium gamma-ethylacetylacetone, chromium gamma-butylacetylacetone, zinc propionylacetone, thallium propionylacetone, cerium propionylacetone, thallium butyrylacetone, and, in general, the reaction products of the metal oxides, hydroxides or salts with beta-diketones, beta-keto-esters, beta-keto-aldehydes, and the like. Thus we may use metal bearing products resulting from the action of the metal hydroxides, oxides, or salts with acetylacetone, benzoylacetone, dibenzoylmethane, acetoacetic esters, methylacetoacetic esters, butylacetoacetic esters, malonic esters, alkylmalonic esters, cyanacetic esters, phloroglucinol, dihydroresorcinol, succina-succinic ester, phenanthrone, camphor, isatin, oxindole, carbostyril, dibenzoylsuccinic esters, diacetylsuccinic esters, benzoylacetic esters, triacylmethanes, dialkyl acetonedicarboxylates, and the like. The alkyl and aryl groups exemplified above may be replaced by sulfur or phosphorus containing alkyl or aryl groups and such sulfur and phosphorus containing compounds, are to be considered as examples of our invention.

Any of these compounds or other members of the classes represented may be used within the scope of our invention; however we have found that the tin compounds, above all, are particularly effective and desirable for our purpose. We therefore prefer them, especially those containing aromatic radicals. The reason for the latter preference is obscure but probably is due to the greater stability of the compounds containing at least one aromatic radical.

The metal enols have varying degrees of solubility in hydrocarbon and other oils. In some cases it is necessary to use a solvent for the compound or to form colloidal suspension of the compound in oil. While some of these compounds have only limited solubility in hydrocarbon oils, it is to be remembered that because of

their great efficiency extremely small amounts are often effective. Thus we may use as little as 0.001 per cent of some of these compounds, and it will be seen that a fairly insoluble material may dissolve to a sufficient extent to be satisfactory for our purpose. In general, more than 0.001 per cent of our addition agents are used; and we may add one, two, or even ten per cent or more.

Furthermore, it is well known that different types of oils have different capabilities of dissolving a given material. For some purposes, therefore, we prefer paraffinic, for other purposes, asphaltic, and for still other purposes, naphthenic or mixed base lubricants. Another method of obtaining a satisfactory mixture of addition agent with the hydrocarbon oil is the use of a mutual solvent to bring the addend into solution. Alternatively, peptizing agents may be added to maintain the metal enol in permanent suspension.

Many of the more difficultly soluble materials are rendered more soluble by the introduction of alkyl groups, particularly those containing four or more carbon atoms. The isoamyl, octyl, lauryl, and octadecyl radicals and radicals from paraffin wax greatly increase the solubility of organic compounds in oil. One or more of such groups may be introduced as required.

It is sometimes advantageous to combine more than one of these compounds in a blend to obtain particular properties. We accomplish this by mixing two or more of these compounds together and blending the mixture with the hydrocarbon oil or by blending one in the hydrocarbon oil, blending the second into this mixture, on so on until the composition is complete.

The various metal enols usually improve both the film strength and oxidation characteristics of the hydrocarbon oil. For example, the sludging tendencies may be decreased by as little as 0.001 per cent of our metal enols. The oxidation characteristics of lubricants are very important, and these are markedly improved by our compounds. The ability to reduce friction is another feature contributed to lubricants by some of our metal enol derivatives.

It may be desirable to include in one and the same blend, in addition to the addends here described, other addends for specific purposes. Thus, we may add a pour point depressor such as a naphthalenechlor wax condensation product, a viscosity index improver such as certain resins or polymerized hydrocarbons, and sulfur or phosphorus containing inhibitors, in addition to our metal enols. Thus we may include such materials as sulfurized methyl esters of corn oil acids, sulfurized (including sulfur-chloride treated) monohydric or dihydric alcohol esters of soybean oil acids, di- and higher polysulfides, such as dibenzyl disulfide, dibenzothiazyl disulfides, amyl polysulfides, dialkyl or aryl xanthates, and the like. Triamyl phosphate, tricresyl phosphate, tri (butylphenyl) phosphite, halogen-bearing phosphates, such as tri-o-chlorophenyl phosphate and mixed phosphates, phosphites, and other esters of phosphorus acids, for example, diphenyl-o-chlorophenyl phosphite, are examples of phosphorus compounds which may be added to blends of our metal enolates. Furthermore, various other metallic and organo-metallic compounds may be added to the blend without interfering with the action of our ingredients. Indeed, in some cases, it is advantageous to combine with our metal enols in a hydrocarbon oil blend such materials as calcium dichlorostearate, chromium oleate, triphenyltin mercaptostearate, aluminum stearate, and others. Various halogenated or halogen-free oxygen bearing ring or aliphatic compounds may be added. For example, we may use chlorodiphenylene oxide, chlorodiphenylether, methyl dichlorostearate, methyl oleate, and the like.

Our addends are admirably adapted for use in lubricating oils of all types including those designed for use in automotive crankcases, Diesel oils, and any other oils of lubricating viscosity. Furthermore, our addends are advantageously blended in gasoline and other petroleum fuels either directly or after being blended first in a lubricating oil and then added to the fuel. Soap-thickened mineral oils of all types ranging from those showing only a slight increase in viscosity over that of the mineral oil alone to the semi-solid and solid greases containing fifty per cent or more of soap are amenable to treatment according to our invention. In making these greases, the usual soaps of sodium, calcium, aluminum, cadmium, antimony, bismuth, lead, etc., such as sodium stearate, aluminum stearate, calcium soaps of beta fat, sodium, aluminum, calcium, cadmium, antimony, bismuth naphthenates and substituted naphthenates, and the like may be used to form the large part of the necessary soap. Various other thickening ingredients or materials for other purposes may be added. These include yarn, hair, graphite, glycerol, water, lamp black, mica, zinc dust, litharge, and the like.

The following examples of blends of our addition agents are given as illustrations and not as limitations:

Example 1

	Per cent
Mid-Continent paraffin base SAE 30	99.0
Stannic acetylacetone dichloride	1.0

Example 2

California naphthenic base SAE 30	98.7
Zinc acetoacetic ester	1.3

Example 3

Paraffin base bright stock	58.0
Paraffin base neutral oil	40.0
Sulfurized methyl esters of corn oil acids	0.1
Stannous propionylacetone	0.2
Calcium dichlorostearate	1.3
Diphenyl-chlor wax condensation product	0.4

Example 4

Mid-Continent paraffin base SAE 40	93.8
Voltolized corn oil	5.0
Chlorodiphenylene oxide	1.0
Chromium gamma-butylacetylacetone	0.2

Example 5

In making a grease containing our addends, we may use:

	Per cent
Oleic acid	8.1
Lime	1.2
Water	0.3
Dichlorostearic acid	1.1
Bright stock	13.1
Distillate (435 seconds at 100° F.)	76.0
Product of reaction of stannic chloride with butylacetoacetic ester	0.2

Example 6

In making a lubricating gasoline, we blend 0.5 per cent of the product of Example 1 with gasoline. The product has the composition:

	Per cent
Gasoline	99.5
Oil	0.495
Stannic acetylacetone dichloride	0.005

It will be understood that certain features and sub-combinations may be employed without reference to other species or combinations. This is contemplated by and is within the scope of our claims. It is further obvious that various changes may be made in details within the scope of our claims without departing from the spirit of our invention. It is therefore to be understood that our invention is not to be limited to the details described.

Having thus described our invention, we claim:

1. A lubricant comprising a major proportion of an oil of lubricating viscosity and a minor proportion of a tin and halogen-bearing reaction product of a stannic halide and a beta-diketone.

2. A lubricant comprising a major proportion of an oil of lubricating viscosity and a minor proportion of stannic bisacetylacetone dichloride.

3. A lubricant comprising a major proportion of an oil of lubricating viscosity and a minor proportion of the tin and chlorine-bearing metal-bearing reaction product of stannic chloride and acetoacetic ester.

4. A lubricant comprising a major proportion of an oil of lubricating viscosity and a minor proportion of stannic bisbenzoylacetone dichloride.

BERT H. LINCOLN.
GORDON D. BYRKIT.