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LUBRICANT AND METHOD OF LUBRICATING

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This invention relates, as indicated, to lubricants and more particularly to compositions for use in connection with the lubrication of relatively moving metallic surfaces and which are especially desirable for internal combustion engines and the like; and it is among the objects of this invention to provide lubricating compositions having certain advantages over such compositions now familiar to those skilled in the art.

As disclosed in issued Patent No. 2,051,744, improved lubricating properties are imparted by halogenated organic compounds having certain characteristics, when added in proper proportions to the ordinary lubricating oils. It has been found, however, that certain subordinate groups or classes of compounds have especial unexpected advantages and, in some instances, the expected desirable characteristics are exhibited to an unexpected degree. The compounds specifically referred to herein constitute such a group or class.

Among the improved lubricating properties above referred to, one of the most notable is the film strength, or extreme pressure characteristics of the lubricant.

By "extreme pressures" are meant pressures of or in excess of about 10,000 lbs. per square inch, such pressures now being commonly encountered in hypoid gears, bearings, contact surfaces of cylinders and piston rings in internal combustion engines, and many other points in machine and structural design. The ordinary mineral oil lubricants satisfactorily affording only thick film lubrication, are unsuited to withstand such pressures and quickly rupture, allowing metal-to-metal contact and consequent disastrous seizure and scoring. Although the thick film be ruptured, it is nevertheless, not entirely destroyed and the metallic bearing surfaces are still affected to some extent by the presence of the lubricant. This condition is commonly referred to as "thin-film" lubrication.

It is among the objects of this invention to provide a lubricating composition and a method of improving the lubricating properties of lubricating oils by improving the thin-film lubricating properties of the oil. I have found that it is possible to so treat the ordinary lubricating oils that seizure and scoring will be prevented at pressures substantially in excess of 10,000 lbs. per square inch and this despite the cessation of ordinary "thick-film" lubrication.

It is another object of this invention to obtain such improved film strength with the aid of halogenated addition agents which will be unusually effective, stable at high temperatures, and inoffensive as to odor.

Another object of this invention is to provide an extreme pressure addition agent which may safely be used in contact with certain types of bearing metals now coming into wide usage, such as those containing a characterizing proportion of copper, silver, lead, nickel or cadmium and the like.

Other objects of the invention will appear as the description proceeds.

To the accomplishment of the foregoing and related ends, said invention, then, consists of the steps hereinafter fully described and particularly pointed out in the claims, the following description setting forth in detail one approved method of carrying out the invention, such disclosed method, however, constituting but one of the various ways in which the principle of the invention may be used.

My invention, broadly stated, contemplates the use in lubricating compositions of halogenated cyclic ketones and the provision of a lubricating composition characterized by the inclusion therein of a minor proportion of a halogenated cyclic ketone, which term is intended to include any halogenated organic ring compound containing a ketone group. More specifically, my invention also contemplates the method of lubricating relatively moving metallic surfaces with a lubricating composition characterized by the inclusion therein of a halogenated cyclic ketone, such addition agent being chemically or physicochemically active on the metallic surfaces to any substantial degree under conditions of extreme pressure or temperature only. Since, in general, the loss of the addition agent by volatilization will be less for compounds having a low volatility, the vapor pressure of the compounds should, for most purposes, be less than atmospheric pressure at temperatures up to 140° C. It is usually desirable, especially for use in internal combustion engines, that the vapor pressure be less than atmospheric at temperatures up to 170° C. In the case of compounds which are stable at temperatures up to their boiling points, this condition may be expressed by stating that the boiling point of the compound should, in general, be higher than 140° C., and for certain uses, such as in internal combustion engines, higher than 170° C.

When used in conjunction with a mineral lubricating oil it is obvious that generally only such amounts of the addition agent may be included as are soluble in the specified amount of oil. By the term "soluble" as herein used I intend to indicate the ability to form not only true solutions but also any form of substantially permanently homogeneous solution when incorporated in mineral oil. With most of the compounds there is usually little difficulty, especially if the incorporation is effected in the manner described in Cornell Patent No. 2,042,880, and since quite small percentages often give remarkably improved results it is seldom of extreme importance that the addition agents be oil soluble in all

proportions. Also, certain compounds are of value as gelling or bodying agents when used in amounts greater than are strictly soluble.

As compounds of the sort included in the present invention are unusually effective as extreme pressure addition agents, for ordinary purposes this invention contemplates the use of not more than 20% by weight, based on the amount of lubricating oil, of such addition agent and amounts as low as 0.1%, and in some cases even less, may be employed with noticeably improved results. From about .25% to about 2.5% is generally a satisfactory range. Very seldom is there any occasion to use more than about 10% of the addition agent.

It should be noted, in addition, that under certain circumstances where little or no thick-film lubrication is required or where the halogenated ketone is a liquid having sufficiently high viscosity at operating temperatures, the halogenated cyclic ketones may be used in a substantially pure state or as the primary lubricating constituent, only that amount of oil being present as may be required to afford the characteristics desired.

All of the halogens are suitable in these compounds but chlorine is the most desirable since it is by far the cheapest and most easily available. Fluorine and bromine are also very effective but somewhat less easily handled. Iodine is relatively expensive and the supply limited but is also effective.

The halogenated aromatic ketones are especially desirable due to their high stability under adverse conditions. They are not easily broken down by high operating temperatures and do not tend to release hydrogen halides which will combine with any moisture present and form destructive acids. This property permits the use of extreme pressure lubricants in contact with many of the alloys now becoming popular for bearings and other uses.

The halogenated aryl ketones are generally preferred, because of their high stability. Alkylation renders certain of them more readily soluble in the ordinary hydrocarbon oils. By alkylation is meant the substitution of an alkyl group for a hydrogen atom of an aromatic radicle. For example, such compounds may be produced from aryl ketones by the Friedel-Krafts or some other condensation reaction. Examples of such alkylated aromatic ketones may be found in the co-pending application of C. F. Prutton, Serial No. 760,038 filed December 31, 1934. As indicated below, by aryl ketones are meant those ketones in which one or both groups are aromatic; and the alkyl-aryl ketones those in which one alkyl group and one aryl group are attached to the same carbonyl group. Chlor-benzophenone is a good example of an aryl ketone which is an efficient addition agent and is readily available.

From a commercial point of view the freedom of the aromatic ketones from objectionable odors is also a valuable asset.

The following list includes some of the most desirable of the halogenated cyclic ketones.

I. Halogenated aromatic ketones:
  A. Halogenated di-aryl ketones, e. g.:
    Halogenated benzophenone.
    Halogenated benzoin.
    Halogenated dinaphthyl ketone.
    Halogenated phenyl naphthyl ketone.
    Halogenated phenyl tolyl ketone.
    Halogenated desoxybenzoin (phenyl benzyl ketone).
    Halogenated benzopinacoline.
    Halogenated dibenzyl ketone.
    Halogenated dixenyl ketone.
  B. Halogenated alkyl-aryl ketones, e. g.:
    Halogenated acetophenone.
    Halogenated butyl phenyl ketone.
    Halogenated dibenzofuryl heptadecyl ketone.
    Halogenated dibenzofuryl undecyl ketone.
    Halogenated phenyl acetone (methyl benzyl ketone).
  C. Halogenated quinones, e. g.:
    Halogenated quinone.
    Halogenated anthraquinone.

II. Halogenated cyclo-aliphatic ketones:
  1. Halogenated cyclopentanone (ketopentamethylene).
  2. Halogenated cyclohexanone.
  3. Halogenated quinone.
  4. Halogenated tetrahydro-quinone.
  5. Halogenated cyclohexyl phenyl ketone (hexahydrobenzophenone).
  6. Halogenated dicyclohexyl ketone (dodecahydrobenzophenone).
  7. Halogenated cyclohexyl methyl ketone (hexahydroacetophenone).
  8. Halogenated cyclohexenyl ketone.
  9. Halogenated camphor.
  10. Halogenated tetrahydro-carvone.

It will be noted that the above list includes examples of the following sub-classes of ketones, all of which are within the scope of the present invention, e. g.:

(*a*) Halogenated ketones in which the ketone group is contained in the ring structure (Examples 1, 2, 3, 4, 9 and 10).

(*b*) Halogenated hydro-aromatic ketones (Examples 5, 6, 7, 8, 9 and 10).

(*c*) Halogenated naphthenic ketones (ketones derived from naphthenic hydrocarbons) (Examples 1, 2, 4, 6 and 7).

(*d*) Halogenated bridged ring ketones (Example 9).

This invention contemplates the use of any number or combination of compounds of the types disclosed in the above lists and such combination may often be preferred.

The halogenated cyclic ketones may usually best be prepared by direct halogenation of the parent ketone as, for example, in the preparation of a chlorinated cyclic ketone by passing chlorine gas into the ketone. The halogenation, or more specifically, chlorination, is usually best carried out at elevated temperatures, say from 50° to 150° C. and in the presence of a catalyst such as iron, iron chloride, phosphorus trichloride, or may be promoted by other suitable means such as actinic rays. In certain cases it may be desirable to use a halogenating agent (e. g. phosphorus pentachloride, PCl_5, or sulphuric oxychloride, SO_2Cl_2) instead of, or in addition to, direct halogenation. After halogenation, the product may be further purified by removal of the hydrogen chloride formed and any untreated chlorine by blowing with air or other inert gas, preferably followed by washing with water or solutions of alkalies or by treatment with solid alkalies such as the hydroxides and carbonates of the alkali and alkaline earth metals.

Since the halogen is the most important film-strengthening factor in the addition agent it is

generally possible to reduce the quantity of addition agent required by increasing its halogen content. For this reason it is often desirable to use cyclic ketones with a halogen content of 50% or more although the presence of much smaller percentages of halogen will generally provide addition agents which are reasonably effective.

The choice of ketone and method of halogenating and purifying will depend largely upon the use to which the finished lubricant in which the product is incorporated as an addition agent is to be put. For use as a gear lubricant or for other purposes where the most important characteristic of the lubricant is its ability to prevent seizing and scoring at high pressures the less stable and more chemically active products are entirely suitable and often preferable. These may be obtained by choosing the cyclo-aliphatic ketones as the starting material or by halogenating a side chain of an alkylated aryl ketone and may also be obtained by halogenating an aryl ketone in such a way as to produce a substantial proportion of halogen addition products in addition to or instead of substitution products. In obtaining more chemically active products, it is best to effect the removal of hydrogen chloride and products which are of too unstable a character to be desirable in the finished product by treatment with alkaline solutions or solid alkaline materials at relatively low temperatures, for example, at a temperature no higher than that to which the finished lubricant will be exposed in service.

For use as a crank case lubricant in internal combustion motors, the more stable and least chemically active products will be preferred. These may usually be best prepared from aromatic ketones by halogenation so that the halogen is attached to a benzenoid ring structure, for example, by using iron as a catalyst and treating with an alkali at elevated temperatures. Where an especially stable product is desired, the product may advantageously be still further purified by distillation. In most cases the distillation may be carried out preferably at reduced pressures, and it is sometimes desirable to distill in the presence of alkaline substances.

The following are given as examples of the preparation of addition agents to be used in a crank case lubricant:

Example A

Benzophenone was chlorinated with iron as a catalyst at a temperature of 90° C. until the gain in weight indicated that about one atom of chlorine had been absorbed per molecule of ketone. The product was then blown with air while maintaining about the same temperature and then subjected to vacuum distillation, the absolute pressure being maintained at about 11 inches of mercury. The distillation temperature was about 280° to 295° C. at the absolute pressure above indicated and about 95% of the product was recovered as the distillate. 5% of anhydrous sodium carbonate in finely divided form was added to the distillate at a temperature of 100° C. and the carbonate and salt allowed to settle out by maintaining the temperature at about 70° C. for 24 hours. Analysis of the resultant product showed that the chlorine content was 14.55% as compared with a theoretical chlorine content of 17.2% in pure monochlor benzophenone.

1% of the resultant product was incorporated in a Pennsylvania S. A. E. 40 motor oil. Tests were performed as shown in Table I. The results obtained with this oil are shown in column A. The same oil with no addition is shown in column O in the same table.

Example B

Benzophenone was chlorinated as before except that the chlorination was continued until approximately 1½ atoms of chlorine per molecule of ketone were absorbed. The purifying steps were similar to those given in Example A with the exception that the distillation pressure was maintained at 1 inch of mercury absolute. At this pressure the distillation temperature was from 239° C. to 243° C. Amount of distillate obtained was approximately 90% of the impure product. After treatment with anhydrous sodium carbonate as in Example A, analysis showed a chlorine content of 22.5% as compared with the theoretical chlorine content of 29.5% in dichlor benzophenone. 1% of this product incorporated in an S. A. E. 40 Pennsylvania motor oil and tested as before gave the results shown under column B of the table.

Example C

Benzophenone was chlorinated as in the previous examples except that about three atoms of chlorine were absorbed per molecule of ketone and the distillation temperature at 1 inch of mercury absolute pressure was 257° to 277° C. Amount of product recovered as distillate in this case was about 85%. After treatment with anhydrous sodium carbonate as in the previous examples, analysis showed a chlorine content of 38.8 as compared with the theoretical chlorine in trichlor benzophenone of 38.6%. 1% of this product added to an S. A. E. 40 motor oil was tested and the results are given under column C of the table.

Example D

½% each of the addition agents prepared as shown in Examples B and C were incorporated in the same Pennsylvania S. A E. 40 motor oil and the results obtained are shown under column D of the table.

TABLE I

[1% of chlorinated benzophenone in Pennsylvania S. A. E. 40 motor oil]

	Example A	Example B	Example C	Example D
Addition agent....None				
Percent Cl in benzophenone	14.55	22.55	38.8	*30.7
"Indiana" oxidation test; viscosity @ 210° F.:				
Original	81.2	79.7	80.0	80.2	79.3
After 100 hrs.	115.5	126.0	132.5	105.1	101.5
Percent increase	42.2	58.0	65.5	31.0	28.0
Conradson Carbon:				
Original	1.32	1.33	1.31	1.30	1.39
After 100 hrs.	3.14	3.73	4.91	3.16	3 03
"Shell" corrosion test; percent change in weight after 192 hrs.:				
Lead-bronze	−0.10	−0.37	−0.13	−0.17	+0.08
Cadmium-silver	−0.03	−0.02	−0.16	+0.20	+0.15
Film strength (Almen), lbs. load at failure	8	15	13	13	14

* Average.

It will be noted from the above examples that the film-strength of the lubricating oil was nearly doubled by additions of but small amounts of the various halogenation products, yet the resultant compositions showed remarkable stability when

subjected to two well-known stringent tests. Thus, in the instance of the lubricant prepared in accordance with Example A, the corrosive effect upon cadmium-silver alloy was actually less than when the plain lubricating oil was used:

The following table shows the comparable results obtained with the same addition agents but using a Mid-Continent oil.

TABLE II

[1% of chlorinated benzophenone in Mid-Continent S. A. E. 30 motor oil]

		Example A	Example B	Example C	Example D
Addition agent	None				
Percent Cl in benzophenone		14.55	22.55	38.8	*30.7
"Indiana" oxidation test; viscosity @ 210° F.:					
Original	65.5	62.3	62.5	62.7	62.6
After 100 hrs.	84.2	84.0	84.2	81.1	72.6
Percent Increase	28.5	34.8	34.7	29.4	16.0
Conradson carbon:					
Original	0.80	0.69	0.64	0.60	0.71
After 100 hrs.	2.83	3.38	3.48	2.86	2.44
"Shell" corrosion test; percent change in weight after 192 hrs.:					
Lead-bronze	0.00	−0.09	−0.20	−0.10	+0.10
Cadmium-silver	−1.06	−0.05	−0.47	−0.45	+0.16
Film strength (Almen), lbs. load at failure	8	14	15	12	16

*Average.

The above examples are merely illustrative and are not intended to limit the scope of this invention in any way nor is this invention restricted to any particular method of preparation of the halogenated cyclic ketone or finished blend.

A lubricating composition comprising a lubricating oil blended with a halogenated cyclic ketone generally has greater thermal stability than the unblended lubricating oil and is therefore particularly suited for use where rather high temperatures will be encountered, as in ordinary internal combustion engines, aviation engines, Diesel engines, and the like.

Lubricating compositions embodying the present invention are desirable in many applications, indeed wherever extreme pressure conditions are encountered, but are of especial advantage in the case of internal combustion engines where high standards of stability and efficiency are required to be met. Although very stable to high temperatures, the halogenated aromatic ketones are unusually efficient as extreme pressure addition agents and but relatively small amounts need be added to the base lubricant. These properties render the resultant lubricating composition especially useful for addition to hydrocarbon fuels, providing safe and adequate lubrication of the upper parts of the engine. An important field of use is in the crankcases and fuels of engines which ordinarily operate under unusually high pressures and at high temperatures such as Diesels and the like. This stability also permits the use of alloy bearings, etc. through a wider range of temperature and pressure conditions than has heretofore been feasible.

Certain of the halogenated aryl ketones, (e. g. 1% of tri-chlorbenzophenone in motor oil) are effective in inhibiting oxidation and sludge formation of oils to which they have been added. Certain of them are also effective pour-point depressors (e. g. halogenated benzophenone which has been alkylated with one or more long-chain radicles) and the same or others also have the property of improving the viscosity index of certain oils to which they may be added. The improvement in lubricating properties resulting from the use of these addition agents is, therefore, not limited to increased film strength, but may extend to other desired characteristics.

While mineral oil generally is the principal ingredient of my lubricant, it is not essential that it be the only ingredient other than my addition agent, provided that there should be no additional ingredient which is incompatible with such addition agent. It is within the contemplation of this invention to include, if necessary or desirable, such other addition agents as are commonly added to improve the viscosity index or cold test of the lubricant and a lubricating composition according to this invention which also has a separate oiliness increasing agent has been found to be unusually effective.

Thus, although the specification refers generally to the halogenated cyclic ketones as addition agents to lubricating oils, it is intended that this description also apply to such lubricants as contain lubricating oils, for example, greases, bodied oils, and the like.

Additional advantages resulting from the use of the halogenated cyclic ketones are the increased oiliness which is imparted to the lubricating composition and the reduced wear of the relatively moving metallic parts which is noted, the working life of such parts being notably extended by the use of the compositions disclosed in the present invention.

Other modes of applying the principle of my invention may be employed instead of the one explained, change being made as regards the materials employed in carrying out the process, provided the ingredient or ingredients stated in any of the following claims or the equivalent of such stated ingredient or ingredients be employed.

I, therefore, particularly point out and distinctly claim as my invention:

1. A lubricating composition comprising a lubricating mineral oil and from about 0.1% to about 20%, based on the amount of mineral oil, of a halogenated hydro-aromatic ketone having a vapor pressure less than atmospheric at 140° C.

2. A lubricating composition containing a lubricating mineral oil and from about 0.1% to about 20% of a halogenated cyclo-hexyl phenyl ketone.

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