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LUBRICATING COMPOSITION CONTAINING SCHIFF BASE-INORGANIC HALIDE ADDUCT

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The present invention relates to a novel Schiff base-inorganic halide adduct and to a lubricating composition containing the Schiff base-inorganic halide adduct to improve the load carrying properties of the lubricating composition.

This application is a continuation-in-part application of application Ser. No. 307,791, filed on Sept. 10, 1963, now Patent No. 3,272,852.

New designs and improvements in machinery are continually raising the operating performance standards of lubricating compositions. In many instances, the pressures and temperatures under which the bearing surfaces of machinery operate are higher than those which natural or synthetic lubricating oils can withstand. Instances where difficult lubricating conditions are encountered occur in the lubrication of heavily loaded pinion and spur gears, gear trains, bearings, extrusion applications and the like. As a result, there is an ever increasing need for lubricating compositions having improved properties for these services.

A novel class of oil-soluble Schiff base-inorganic halide adducts has been discovered which imparts greatly improved properties to lubricating oils. The lubricant compositions containing the adducts are particularly notable for their improvement in load carrying and anti-scuff properties although they also exhibit additional valuable features, such as corrosion resistance, oxidation resistance and stability. The Schiff base-inorganic halide adducts are also useful as insecticides, fungicides, bactericides and in the preparation of pharmaceuticals.

The novel oil-soluble adduct of the invention is formed from the reaction of a Schiff base and an inorganic halide. This adduct is represented by the following formula:

$$(RN{=}\overset{H}{C}R')_y{\cdot}MX_z$$

wherein R is a hydrocarbyl radical having from 1 to 30 carbon atoms, R' is hydrogen or a hydrocarbyl radical having from 1 to 18 carbon atoms, the sum of the carbon atoms in R and R' being at least 12, y is an integer from 1 to 6, M is a polyvalent cation selected from the class consisting of boron, aluminum, titanium, tin, zinc, copper, cadmium, magnesium, mercury, zirconium, antimony, bismuth, manganese and iron, X is a halide ion selected from the group consisting of chloride, bromide, and iodide ions and in the case of divalent tin and the cations having a valence of 3 to 4 the fluoride ion, and z is an integer from 2 to 4 equal to the valence of M.

The novel lubricating composition of the invention comprises a major proportion of a lubricating oil base and a minor amount of the adduct described above. Mineral and synthetic lubricating oil bases can be employed to prepare a lubricating composition containing the adduct.

The Schiff base which corresponds to the formula:

$$RN{=}\overset{H}{C}R'$$

in which R and R' have the values noted above and which is employed to form the adduct of the invention is prepared from an amine and an aldehyde. Specifically, equivalent amounts of a primary amine and an aldehyde are contacted either in the presence of or without a solvent. This reaction frequently occurs spontaneously although at times moderate heating is required. The reaction causes a mole of water to split out in the formation of the Schiff base. The water formed by the reaction is generally removed by azeotroping with a solvent, such as toluene. It is essential that the sum of the carbon atoms represented by R and R' in the formula for the Schiff base amount to at least 12 in order to insure the oil solubility of the adduct that is ultimately formed.

Amines which can be employed to prepare the Schiff base are the primary aliphatic amines. These amines are represented by the following formula:

$$RNH_2$$

in which R is an aliphatic hydrocarbyl radical having from 1 to 30 carbon atoms. The preferred amines are those in which R is a branched chain alkyl radical having from about 12 to 24 carbon atoms.

Examples of suitable amines include butylamine, amylamine, hexylamine, octylamine, laurylamine, tridecylamine, tetradecylamine, hexadecylamine, octadecylamine and tricosylamine. Particularly preferred amines are certain commercially available mixtures of tertiary alkyl primary amines. For example, a mixture of tertiary alkyl primary amines in which the alkyl radical comprises a mixture of alkyl groups having 11 to 14 carbon atoms is available under the name "Primene 81–R". Another commercially available amine is the mixture of tertiary alkyl primary amines in which the alkyl radical comprises a mixture of alkyl groups having 18 to 24 carbon atoms which is available under the name of "Primene JM–T."

Aldehydes which can be employed to react with the primary amines in forming the Schiff base are represented by the following formula:

$$R'CHO$$

in which R' is hydrogen or a hydrocarbyl radical having from 1 to 18 carbon atoms. The hydrocarbyl radical can be an aliphatic or an aromatic hydrocarbyl radical and preferably has from 1 to 10 carbon atoms. Examples of aldehydes which can be employed include formaldehyde, 2-ethylhexaldehyde, acetylaldehyde, propionaldehyde, butyraldehyde, nonylaldehyde, palmitic aldehyde, lauraldehyde, stearaldehyde and benzaldehyde.

The following examples are typical of the method of preparing the Schiff base.

Example I

256 g. 2-ethylhexaldehyde (2 moles) were added slowly to 630 g. (2 moles) "Primene JM–T" (C_{18-24} tertiary alkyl primary amine) in a stirred flask. The reaction was moderately exothermic. Toluene (150 ml.) was added and the mixture heated to reflux. Water (30 ml.) was recovered equivalent to 83% of theoretical. The toluene was removed using a stream of nitrogen, and 836 g. clear amber Schiff base were obtained.

Example II

344 g. of a 35% aqueous solution of formaldehyde (4 moles CH_2O) were added slowly to 1260 g. "Primene JM–T" (4 moles) in a stirred flask. The reaction was mildly exothermic. Toluene (300 ml.) was added and the mixture heated to reflux. The theoretical amount of water (296 ml.) was recovered. Toluene was stripped with the aid of a stream of nitrogen to yield 1274 g. of clear, amber Schiff base.

The adducts of the invention are prepared by mixing a Schiff base defined above with an inorganic halide compound from the class set forth. The reaction is usually exothermic and provision must generally be made for cooling the reaction mixture. Caution must be exercised to keep the reaction temperature below the decomposition temperature of both components of the reaction product

which generally means conducting a reaction at a temperature below about 200° C. The reaction generally goes to completion in a short reaction time.

Halides of metals and metalloids which can be employed to react with the Schiff base and to form the load carrying adducts of the invention include boron trifluoride, boron trichloride, aluminum trichloride, aluminum trifluoride, titanium tetrachloride, titanium tetrafluoride, stannous chloride, stannous fluoride, stannic chloride, cupric chloride, cupric bromide, cadmium chloride, cadmium iodide, magnesium chloride, mercuric chloride, zirconium chloride, antimony chloride, antimony fluoride, bismuth chloride, manganese chloride, and ferric chloride. The preferred halides are those formed from titanium, tin, antimony, copper and zinc.

Only specific halides as set forth above are effective for producing the adducts of the invention. Examples of halides which do not form adducts include cuprous chloride, cupric fluoride, magnesium fluoride, manganous fluoride, antimony oxychloride, barium chloride, lithium chloride and calcium chloride.

An unexpected phenomenon is the discovery that the inorganic salt must have a substantial and apparently a critical degree of water solubility in order to form a complex with an amine of the type disclosed herein. The reason for the relationship between water solubility and complex formation is not fully understood. It has been determined, however, that the following critical conditions must be met in order to form a complex of the type disclosed:

A. The metallic element of the salt must be capable of sharing the unpaired electron of the amine nitrogen.

B. The salts must have a water solubility greater than 0.2 mole per liter at a temperature in the range of 15–100° C.

Examples of inorganic salts and their behavior toward complex formation with a C_{21} primary amine ("Primene JM–T") is given in Table I below:

TABLE I

Salt	H_2O Solubility, Mols Salt/l. of H_2O	Complex Formation With C_{21} Primary Amine
$ZnCl_2$	45.3 (100° C.)	Yes.
ZnF_2	0.15 (95° C.)	No.
$SnCl_2$	14.2 (15° C.)	Yes.
SnF_2	2.68 (18° C.)	Yes.

The Schiff base and halide are reacted in the proportion of 1 to 6 moles of Schiff base to 1 mole of the halide compound with the preferred amount of the Schiff base being from 1 to 4 moles.

The following examples are typical of the method of preparing the adduct.

Example III

15.7 g. (0.1 mole) SNF_2 were added to 66 g. (0.2 mole) of the Schiff base of Example II. 50 ml. acetone were added and the mixture stirred until thoroughly mixed. Heating and stirring at a maximum temperature of about 60° C. were continued for 18 hours. The slightly hazy product was filtered, leaving a residue of less than 1 g.

Example IV

2.4 g. (0.02 mole) TiF_4 were dissolved in 50 ml. acetone and the solution added to 33.5 g. (0.08 mole) of the Schiff base of Example I. The acetone was removed on steam bath. The slightly hazy viscous orange colored liquid was filtered to give a TiF_4 complex of the Schiff base.

Examples of adducts of the invention are given below. For additional convenience, the Schiff base part of the adducts is expressed in terms of the components from which the Schiff bases are formed. The mole ratio in brackets is the ratio of the Schiff base to the inorganic halide.

"Primene JM–T"/formaldehyde:boron trifluoride (3:1),
"Primene JM–T"/formaldehyde:boron trichloride (3:1),
"Primene JM–T"/formaldehyde:aluminum trichloride (3:1),
"Primene JM–T"/formaldehyde:tin tetrachloride (4:1),
"Primene JM–T"/2-ethylhexaldehyde:antimony trifluoride (2:1),
"Primene JM–T"/2-ethylhexaldehyde:titanium tetrafluoride (4:1),
"Primene JM–T"/formaldehyde:stannous fluoride (2:1),
"Primene 81–R"/formaldehyde:cadmium chloride (2:1),
"Primene 81–R"/formaldehyde:cadmium iodide (2:1),
"Primene 81–R"/formaldehyde:zirconium chloride (2:1),
"Primene 81–R"/formaldehyde:bismuth chloride (2:1),
"Primene JM–T"/formaldehyde:cupric chloride (2:1),
"Primene JM–T"/formaldehyde:magnesium chloride (2:1),
"Primene JM–T"/2-ethylhexaldehyde:mercuric chloride (2:1),
"Primene JM–T"/2-ethylhexaldehyde:manganous chloride (2:1),
"Primene JM–T"/2-ethylhexaldehyde:ferric chloride (2:1),
"Primene JM–T"/formaldehyde:zinc chloride (2:1), and
"Primene JM–T"/2-ethylhexaldehyde:stannous chloride (2:1).

The lubricating compositions of the invention are prepared by blending in a conventional way a minor amount of the oil-soluble, load carrying Schiff base-inorganic halide adduct described hereinabove into a suitable lubricating oil base. Generally, the adduct is employed in an amount in the range of 0.05 to 10 percent by weight based on the weight of the lubricating composition with the preferred proportions of the adduct being from 0.1 to 3 weight percent.

The base lubricating oil can be a mineral lubricating oil or a synthetic lubricating oil. The mineral lubricating oil can be a predominantly paraffinic or naphthenic oil or it can be a mixture of both types of mineral oils. Generally, the mineral oil will be a refined oil of predominantly paraffinic nature having a viscosity in the range from 30 to 150 Saybolt Universal seconds at 210° F.

Various types of synthetic lubricating oil bases can be employed in preparing the lubricants of the invention. Aliphatic ester, polyalkylene oxides, silicones, esters of phosphoric and salicyclic acid and the highly fluorine-substituted hydrocarbons can be employed. Examples of the aliphatic esters include di-(2-ethylhexyl) sebacate, the dialkyl azelates, dialkyl suberates, and the dialkyl adipates such as di-hexyl azelate, di-(2-ethylhexyl) azelate, di-3,5,5-trimethylhexyl glutarate, di-(2-ethylhexyl) adipate, tri-amyl tricarballylate, etc. The polyalkylene oxides include polyisopropylene oxide, polyisopropylene oxide diether, polyisopropylene oxide diesters, etc. The silicones include methyl silicone, methylphenyl silicone, and the silicates include tetraisooctyl silicate. The highly fluorinated hydrocarbons include fluorinated oil, perfluorohydrocarbons, etc.

Other effective synthetic lubricating oils include the neopentyl glycol esters such as the neopentyl glycol propionates, neopentyl glycol butyrates and neopentyl glycol caprylates and the trimethylol alkanes such as trimethylol ethane, trimethylol propane, trimethylol pentane, trimethylol heptane and trimethylol dodecane and the like. Examples of the phosphate esters include tricresyl phosphate, trioctyl phosphate and tridecyl phosphate as well as mixed aryl and alkyl phosphates.

Example V

The load carrying and anti-scuff properties of lubricating compositions of the invention was determined in the mean Hertz load test. This test is run in a machine having four ½ inch diameter bearing balls which are driven under load while being lubricated by the composition under test. The description of this test is set forth in U.S. Patent 2,600,058.

The Schiff base A designation referred to in the following compositions was prepared by reacting a mole of "Primene JM–T" with a mole of 2-ethylhexaldehyde. Schiff base B refers to the Schiff base prepared by the reaction of a mole of "Primene JM–T" with a mole of formaldehyde.

The lubricating compositions tested were prepared using both mineral and synthetic base oils. Base oil A was a commercially available synthetic lubricating oil consisting of di-2-ethylhexyl sebacate plus sebacic acid and having an SUS viscosity at 100° F. of about 70. Base oil B was a mineral lubricating oil having an SUS viscosity at 210° F. of about 100. The lubricant compositions of the example contained 1 percent by weight of the indicated Schiff base-halide adduct. The results of this test are given in Table II below.

TABLE II.—LOAD CARRYING AND ANTI-SCUFF PROPERTIES

Lubricant Composition	Adduct Mole Ratio	Mean Hertz Load
Base Oil A		16
Base Oil A plus Schiff Base A/SbF_3	(2:1)	57
Base Oil A plus Schiff Base A/TiF_4	(2:1)	23
Base Oil A plus Schiff Base B/SnF_2	(2:1)	31
Base Oil B		27
Base Oil B plus Schiff Base B/$SnCl_2$	(2:1)	44

The test results show that the lubricating compositions of the invention were substantially improved with respect to their load carrying and anti-scuff properties. The load carrying properties of the oil tested are particularly valuable in lubricants adapted for use in gas turbines.

Example VI

The load carrying and anti-scuff properties of lubricant compositions containing different percentages of the adduct of "Primene JM–T"/2-ethylhexaldehyde Schiff base with titanium tetrafluoride was determined in the Ryder gear test. In the Ryder gear test (Federal Test Method 6508) the lubricant is employed to lubricate two spur gears in a Pratt and Whitney gear and lubricating tester. This tester was operated with a gear speed of 10,000 r.p.m. and with an oil inlet temperature of 165° F. A loading pressure of 5.0 p.s.i. was applied during break-in. After 10 minutes the tester was shut down and the gear examined for the percentage of tooth area scuff on each tooth. The procedure was then repeated using a high load pressure with increments of 5 p.s.i. until 22.5 percent of the total tooth area on the driving gear had been scuffed, the load applied in this run being considered the scuff load. The tooth load in pounds per inch of tooth width was then calculated. The base oil employed was the same as base oil A employed in Example V above. The results of this test are given in Table III.

TABLE III.—LOAD CARRYING AND ANTI-SCUFF PROPERTIES BY THE RYDER GEAR TEST

Oil composition (wt.):	Ryder gear test, p.p.i.
Base oil	2300
Base oil+1% Schiff base/TiF_4	4320+
Base oil+.5% Schiff base/TiF_4	4350+
Base oil+0.1% Schiff base/TiF_4	3980

The lubricating compositions containing the above-described Schiff base-inorganic halide adducts have markedly improved load carrying and anti-scuff properties. They also exhibit good corrosion resistance, oxidation resistance and storage stability. These valuable properties make the lubricants of the invention suitable for a broad range of lubrication applications.

It is understood that the lubricating compositions of the invention can contain numerous additives conventionally used to improve the properties of lubricating oils. Commonly employed additives are the methacrylates as V.I. improvers and pour point depressors, the alkylphenols as oxidation inhibitors, alkaline earth metal salts of petroleum sulfonates or alkaryl sulfonates as detergents, metal dialkyl dithiophosphate corrosion inhibitors and silicone anti-foam fluids.

Obviously, many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof and, therefore, only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. A lubricating composition comprising a major proportion of a lubricating oil and 0.05 to 10 percent by weight of an oil-soluble adduct of a Schiff base and a halide having the formula:

$$(RN{=}\overset{H}{C}R')_y{\cdot}MX_z$$

in which R is an alkyl radical having from 1 to 30 carbon atoms, R' is selected from the group consisting of hydrogen and an alkyl radical having from 1 to 18 carbon atoms, the sum of the carbon atoms in R and R' being at least 12, y is an integer from 1 to 6, M is a polyvalent cation selected from the class consisting of boron, aluminum, titanium, tin, zinc, copper, cadmium, magnesium, mercury, zirconium, antimony, bismuth, manganese and iron, X is a halide ion selected from the group consisting of chloride, bromide and iodide ions and in the case of divalent tin and the cations having a valence of 3 to 4 the fluoride ion, and z is an integer from 2 to 4 equal to the valence of M.

2. A lubricating composition according to claim 1 in which M is titanium.

3. A lubricating composition according to claim 1 in which M is tin.

4. A lubricating composition according to claim 1 in which M is zinc.

5. A lubricating composition according to claim 1 in which M is copper.

6. A lubricating composition according to claim 1 in which M is antimony.

7. A lubricating composition according to claim 1 in which MX_z is titanium tetrafluoride.

8. A lubricating composition according to claim 1 in which MX_z is stannous fluoride.

9. A lubricating composition according to claim 1 in which MX_z is antimony trifluoride.

10. A lubricating composition according to claim 1 in which MX_z is aluminum trifluoride.

11. A lubricating composition according to claim 1 in which said halide has a water solubility greater than 0.2 mole per liter at a temperature in the range of 15–100° C.

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