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LUBRICATION OF SPECIAL ALLOY BEARINGS

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This invention relates to improvements in the lubrication of special alloy bearings; and it comprises methods of lubricating special alloy bearing surfaces in internal combustion engines when subjected to conditions of operation, namely, high bearing temperatures, pressures and speeds, by maintaining between the bearing surfaces, one of which is an alloy formed chiefly of a metal consisting of the class cadmium and copper, a film of lubricating oil which initially produces an effective lubricating action but which would normally tend to corrode the aforesaid alloys, and maintaining the effectiveness of the lubricating oil by incorporation therein a di-alkyl polysulfide, specifically di-amyI tri-sulfide or tetra-sulfide, in a small amount but sufficient proportion to substantially retard said corrosion, and it also comprises improved lubricating compositions and lubricants containing sufficient amounts of said di-alkyl polysulfides to mitigate or retard the normal destructive action of the lubricating oil upon said bearing surface, these improved lubricants being useful in lubricating the alloy bearings of internal combustion engines when subjected to the said conditions of operation; all as more fully hereinafter set forth and as claimed.

Recent developments in the design of mechanical equipment for generating and transmitting power, and particularly in the automotive field, have necessitated new bearing metals with special properties. Among these new bearing materials are binary and ternary alloys of the metals mentioned above. Cadmium-silver-copper, cadmium-nickel-copper, copper-lead-nickel, etc., alloys are in use. One ternary alloy currently used in automobile engines is an alloy of cadmium with minor amounts of both silver and copper. Under the conditions imposed by modern engineering design these new alloy bearings are commonly subjected to more severe operating conditions than were usual in the older art: to higher bearing loads, higher rubbing speeds and higher temperatures of operation. It is found that in actual use under these conditions there often develops serious destructive action on the bearing surface by mineral lubricating oils, even by those standard commercial oils giving particularly good results with the older bearing metals under the earlier operating conditions. The destruction of the bearing metal probably results from action of deterioration products developed in the oil. An object achieved in the present invention is the production of lubricating oils improved for these newer conditions of use and which are characterized by reduction or elimination of destructive action on

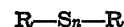
the newer bearing metals by deterioration products in the oil.

We have discovered that the organic polysulfides, such as tri-sulfides, tetra-sulfides, etc., incorporated with lubricants, are capable of achieving the objects of the present invention, the di-alkyl polysulfides, such as those containing the various amyI groups, being particularly effective. By adding small amounts of such compounds to the mineral oil or lubricant, we obtain improved lubricating compositions which satisfactorily lubricate alloy bearings. Incorporated in mineral oil, these compounds retard destruction of the bearing metal. The character and amount of the added improvement agents, here employed, are such that the normal physical properties of the oil, such as viscosity, gravity, color, etc., are not substantially altered. Certain properties of the lubricant are improved without sacrificing the other desirable properties.

We obtain improved mineral oils and lubricants suitable for lubricating bearings under a wide range of service conditions. The new compounded lubricant satisfactorily lubricates the new alloy bearings even under high unit pressure, high bearing speeds and high operating temperatures. When prepared from suitable motor oils, the present improved compositions are excellent lubricants for the modern automobile engine. They satisfactorily lubricate the bearings without any destruction of the special bearing alloys now used, even in the presence of a free circulation of air.

We have found that between 0.05 and 0.50 per cent of these di-alkyl polysulfides when dissolved in mineral lubricating oils are sufficient to produce satisfactory lubricants for the said alloy bearings and that the lubricants so obtained are particularly useful for lubricating internal combustion engines without corroding such bearings. The particular proportions depend upon the particular improvement agent and lubricating base employed. As the lubricating base there may be employed any of the usual motor oils.

The organic polysulfides here employed to improve mineral oils and lubricating compositions may be represented by the following formula:



wherein n is 3 to 4 and R represents an alkyl group. As a class, these di-alkyl polysulfides are soluble and miscible with mineral oils in substantial proportions. We have found that they are sufficiently soluble and miscible to permit incorporation with the mineral oil, of an amount of

organic polysulfide sufficient for the present purposes.

These organic polysulfides may be readily prepared by reacting various commercial sulfur chlorides with suitable mercaptans, such as aromatic or aliphatic mercaptans.

In preparing these organic polysulfides, either a relatively pure mercaptan or a commercial mixture of mercaptans may be employed. The commercial alkyl mercaptans are ordinarily employed as they yield organic polysulfides advantageous for the present purposes. Commercial amyl mercaptan is a typical alkyl mercaptan and being readily available as a commercial material is ordinarily employed. The commercial preparation, in addition to the normal amyl compound, usually contains all of the possible amyl isomers and may be used for making mixed organic polysulfides desirable for the present purposes. There are some specific advantages both in n-amyl and iso-amyl compositions. The same is true of the compounds derived from the butyl and propyl mercaptans; each has specific advantages in certain relations.

Thus, while amyl mercaptan is ordinarily used in the present invention, other specific alkyl mercaptans such as the ethyl, butyl and propyl mercaptans may also be used to advantage. Also, we use the natural mercaptans obtained from mineral oils such as those derived from the lighter fractions thereof. In various refining methods such mercaptans are isolated from the oil. Any of these mercaptans may be reacted with sulfur chloride to prepare organic polysulfides satisfactorily for the present purposes.

These mercaptans may be converted into organic polysulfides advantageous for the present purposes by reaction with any of the usual sulfur chlorides such as sulfur-mono-chloride (S_2Cl_2), sulfur di-chloride (SCl_2), etc., or mixtures thereof. Ordinarily, the commercial sulfur chlorides are used in the general practice of our invention. Substantially pure sulfur mono-chloride has a light yellow color. The usual commercial sulfur mono-chlorides are yellowish-red heavy liquids. Commercial sulfur dichloride is a dark brownish-red liquid. However, most commercial preparations are more or less mixtures of various sulfur chlorides in equilibrium with each other; they primarily being composed of sulfur dichloride and sulfur mono-chloride, depending upon the commercial source of the preparation, and other sulfur chlorides such as sulfur tetra-chloride (SCl_4) and sulfur tritetrachloride (S_3Cl_4) may also be present. Advantageously, commercial sulfur chloride preparations having the following properties may be employed in the practice of this invention:

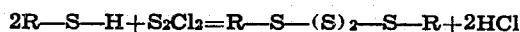
Specific gravity: 15°/15° C	1.6 to 1.7
Melting point: °C	-78 to -80
Boiling range: °C	59 to 139
Color	Light yellow to dark red
Sulfur: per cent	31.1 to 47.4
Chlorine: per cent	68.9 to 52.6

Sulfur mono-chloride and sulfur dichloride when reacted with mercaptans primarily yield tetra-sulfides and tri-sulfides, respectively. However, the tri-sulfides and the tetra-sulfides may condense or polymerize to form higher sulfides such as hexa-sulfide, etc., possibly due to the oxidizing influence of an excess of sulfur chloride in the earlier stages of the reaction.

Thus the mixtures of organic polysulfides here obtained, while they are usually composed pri-

marily of organic open chain polysulfides, sometimes contain other polysulfides. For instance, only a part of the sulfur atoms may be divalent or more than one organic radical may be attached to a particular sulfur atom. The latter type of compound is generally formed when some sulfur tetra-chloride is present. Thus in such mixtures some of the polysulfides contain only divalent sulfur, whereas others may contain both divalent and tetravalent sulfur and have a complex sulfur nucleus.

The reaction between sulfur mono-chloride and alkyl mercaptans is typical and the following equation representing that reaction illustrates the method of forming the organic polysulfide:



the other sulfur chlorides likewise form organic polysulfides by the above reactions.

In commercial practice, we employ sufficient sulfur chloride to convert substantially all of the mercaptan into the desired polysulfide, it being advantageous to employ a slight excess of the sulfur chloride to insure complete reaction. Ordinarily, the sulfur chloride is gradually added to the mercaptan and after the reaction has been completed, the slight excess of unreacted sulfur chloride is removed in recovering the organic polysulfide for use in making improved lubricants.

The reaction between the sulfur chloride and the mercaptan being an exothermic reaction, it is here effected under controlled conditions. We have found it best to maintain the initial reaction temperature below about 100° F., for instance, between 40° and 90° F. during the primary stages of the reaction. To maintain the reaction temperature within the desired range, the sulfur chloride is gradually added to the mercaptan at such a rate as to prevent an excessive rise in the initial temperature; the rate of addition being such that ordinarily the temperature is about 80° F. or slightly higher, during the primary stages of the reaction. Ordinarily external cooling is advantageous to hold the temperature in check, and the mercaptan may be pre-cooled to about 40° F., before the sulfur chloride is introduced. When high temperatures occur during the initial or primary stages of the reaction, undesirable by-products or side reaction products are formed, which results in a reaction product which is ineffective and otherwise undesirable for the present purposes.

After all the sulfur chloride has been added and reaction has been effected, two to four hours being ordinarily required due to slowly contacting the reactants, the reaction mixture is heated to somewhat higher temperatures, say between 200° and 250° F. for the secondary stages of the reaction and held at that temperature until the residual reactants and undissolved hydrochloric acid is removed. The hydrogen chloride formed as a by-product is mainly evolved as a gas during this heating. Any residual hydrochloric acid remaining in the poly-sulfides after heating may be removed by washing and neutralization. In purifying the organic polysulfides they may be washed with water to remove the excess sulfur chloride and other unreacted products. If further purification is desired, the polysulfides may be washed with a weak alkaline solution such as sodium carbonate to completely neutralize and remove the last traces of acid constituents. The organic polysulfides thus obtained from amyl mercaptans are oils having a pleasant odor.

They are quite soluble and miscible with mineral oil.

While the polysulfides of the lower molecular weight hydrocarbons are non-viscous oily liquids, the polysulfides of higher molecular weight are solids having a relatively low melting point, most of this melting between 30° and 80° C. In practicing the present invention the organic trisulfides, tetra-sulfides and penta-sulfides are advantageous. These may be represented by the following general formula:



wherein n is 3 to 6. As stated ante, dialkyl polysulfides are particularly advantageous. These may be represented by the following formulae:

Di-alkyl tri-sulfide



Di-alkyl tetra-sulfide



Di-alkyl penta-sulfide



In the practice of this invention we may use relatively pure individual organic polysulfides or mixtures of such polysulfides. For instance, mixtures of tri-sulfide and tetra-sulfide, etc., may be employed in commercial practice.

The amyl polysulfide obtained from commercial amyl mercaptan is a reddish-yellow oil of pleasant odor and has the following properties:

Gravity: API.....	2.0
Viscosity.....	Non-viscous
Sulfur: percent.....	44.3

It may be obtained by reacting commercial amyl mercaptan with sulfur mono-chloride, S_2Cl_2 . This amyl polysulfide is advantageous in the present invention. Other specific alkyl polysulfides which are advantageous for improving petroleum oils and mineral oil lubricants are the ethyl, propyl and butyl polysulfides. Generally we have found that organic polysulfides having properties within the range set forth in the following table are advantageous for the present purposes:

Gravity: API.....	1.0-10.0
Viscosity.....	Non-viscous
Sulfur: percent.....	40-55

These alkyl polysulfides are insoluble in water and in aqueous solutions and therefore the compounded lubricants prepared from them are not easily emulsified with water. All of them are quite stable even at elevated temperatures; and they are particularly so at the operating temperatures usually encountered in the lubrication of alloy bearings. Also, they are substantially neutral in reaction. As stated ante, most of them are oily liquids at normal temperatures, although some are solids melting at relatively low temperatures. Generally, their color varies from a pale yellow to a reddish-yellow and when dissolved in the mineral oil the oil is only slightly colored; the slight yellowish color imparted to the oil sometimes being advantageous.

Generally the dialkyl polysulfides are readily miscible and compatible with petroleum oils in the percentages necessary for the present purposes. They may be incorporated with the mineral oil or lubricating base in any suitable manner. They may be dissolved in the oil by simply mixing the organic polysulfide with the oil and slightly warming with agitation to obtain uniform lubricants. Warming the oil to temperatures

between 160° and 180° F. is sufficient to dissolve even the solid compounds; they being readily soluble in the warm oil. With the heavy and more viscous lubricating oils this warming is advantageous since the heating lowers the viscosity of the oil facilitating the blending. In some cases these compounds may be dissolved in suitable volatile solvents and the solution thereof added to the oil, the solvent being subsequently distilled off. This solvent method is particularly effective with the solid organic polysulfides. Also, they may be first dissolved in a suitable lubricating oil to form a master batch which is subsequently blended with more lubricating or motor oil to give a range of lubricating compositions as desired. Likewise, the compounded lubricant may be converted into thickened compositions or greases in any of the usual ways. Sometimes the improvement agent may be directly added to metal soap greases or other compounded lubricants in which the petroleum oil is the lubricating base.

In the practice of the present invention any suitable mineral lubricating oil base may be employed, either heavy or light oil. Ordinarily it is best to select a good grade of mineral lubricating oil which has suitable initial properties for the particular lubrication requirement. Then the addition of the improvement agent produces additional desired advantages, including extreme pressure characteristics, restrained destructiveness toward the newer alloy bearing metals, etc. That is, petroleum oils and lubricants of the usual grades may be employed in practicing this invention. The oils having properties classifying them as motor oils of SAE 10, 20 and 30 are advantageous. Likewise, special lubricants such as obtained by blending certain non-mineral oils with the mineral oil may be improved by the addition of these compounds.

The deterioration of bearings by particular oils under drastic service conditions may be readily observed by visual inspection, but a special laboratory test is necessary to readily and quickly determine this on a standard comparable and reproducible basis and to readily evaluate commercial lubricants for such alloy bearings. We have devised a satisfactory accelerated test procedure which is as follows.

An alloy bearing shell of certain commonly used standard dimensions is submerged in 300 cc. of the oil or oil composition in a 400 cc. Pyrex beaker and heated in a thermostatically controlled oil bath to 175° C. (347° F.) and air, at the rate of 2000 cc. per hour, is bubbled through the oil in contact with the bearing shell. At the end of 48 and 96 hours, the loss of weight and the condition of the bearing shell are determined. In determining the loss in weight the bearing shell is washed free of oil and dried before weighing. This test will hereinafter be referred to as our standard laboratory test.

When determining the effectiveness of various improvement agents the usual procedure is to run a "blank" test simultaneously with the oil composition being tested, employing for that purpose a sample of the untreated oil.

In such tests it is advantageous to employ commercial bearing shells. These shells comprise a suitable metal backing faced with the alloy bearing metal. In the above test, the air is bubbled against the alloy bearing face. In this way, the actual bearing face is subjected to severe deteriorative conditions. By comparison of the results of such tests with actual service tests, we have

found them to be in substantial agreement as to the suitability of particular lubricants.

In testing our lubricants, we have employed, among others, bearings of the following approximate composition:

1. Cadmium-silver alloy

	Metal	Per cent
0	Cadmium.....	98
	Silver.....	1
	Copper.....	1

2. Lead-copper alloy

	Metal	Per cent
5	Lead.....	45
	Copper.....	53
0	Nickel.....	2

Such alloys are used in the tests to determine the properties of improved lubricants given post. In such tests the loss in weight, while not extremely high when expressed as "per cent loss", is nevertheless very significant, as the bearing shells used have an alloy facing of only .008 inch to .012 inch thickness on a highly resistant backing and the observed losses in the reported tests often represent a loss of the order of ten per cent of the alloy facing.

The specific examples and tests given post are illustrative of detail embodiments of the present invention.

EXAMPLE 1.—The following example illustrates one method of preparing the improvement agent from commercial grades of amyl mercaptan and of sulfur mono-chloride; commercial materials having the following properties being employed:

Amyl mercaptan

0	Molecular weight.....	104
	Distillation range: °C.....	104–127
	Specific gravity 20/20° C.....	0.83–0.84
	Vapor pressure: 22° C.....	29 mm.
5	Flash, O. C.: °C.....	38–34

Sulfur mono-chloride

	Specific gravity: 29° C.....	1.645
	Boiling range: °C.....	136–140
0	Color.....	Light yellow
	Sulfur: per cent.....	47.4
	Chlorine: per cent.....	52.6

Into a suitable vessel there are introduced two mols of said amyl mercaptan. Then one mol of sulfur chloride (S₂Cl₂) is gradually added with stirring to the mercaptan so that the exothermic heat of reaction brings the mixture to about 60° F. and the remainder of the sulfur chloride is slowly added to the reaction mixture at such a rate that the temperature remains somewhat above 70° F. but does not exceed 90° F. About two to four hours is required to so add the sulfur chloride. After the exothermic reaction has subsided then the reaction mixture is heated to about 250° F. and maintained at that temperature until the reaction is complete. During this time the by-product hydrogen chloride is evolved as a gas and removed and collected in a suitable container. The principal reaction product so obtained is a reddish-yellow oil of pleasing odor and contains a mixture of di-amyl polysulfides of which the tetra-chloride is a major component.

The amyl polysulfides so obtained are freed of

excess sulfur chloride and other unreacted reagent as well as residual HCl by washing with water. In this operation the oil obtained as above is stirred with about 50 per cent by volume of warm water and then the oil and water permitted to stratify. The oil is separated from the water and then washed with 10 per cent by volume of a weak sodium carbonate solution, the oil being again stratified and separated from the aqueous solution. If desired it may be again washed with warm water. After being so washed, the oil is then dried. To dry the oil a current of warm air may be blown through the oil until dry. The purified reddish-yellow oil so obtained has the following properties:

Gravity: °API.....	2.0
Viscosity.....	Non-viscous
Sulfur: per cent.....	44.3

EXAMPLE 2.—Into a suitable vessel there are introduced 1000 gallons (7200 lbs.) of Pennsylvania motor oil SAE 10 grade and the oil warmed to 165° F. Then 7.2 pounds of the amyl polysulfide obtained in Example 1 (0.10 per cent by weight of the oil) are gradually added and the mixture agitated by passing a current of air through the same until a uniform blend is obtained, about 1 hour being required.

The properties of the original and improved motor oil are as follows:

Table A

	Original oil	Improved lubricant
Gravity, °API.....	32.8	32.8
Viscosity, SUV:		
100° F.....	184.2	184.0
210° F.....	46.4	46.3
Flash, O. C.: °F.....	430	430
Fire, O. C.: °F.....	490	490
Pour, °F.....	+5	+5
Color: NPA.....	1.25	1.50
Carbon residue.....	0.01	0.02
Copper strip.....	Satisfactory	Satisfactory

From the above table, it is clear that the addition of the alkyl polysulfides does not substantially change the ordinary properties of the oil. However, the improved lubricant obtained is substantially non-corrosive to alloy bearings. When tested by the standard laboratory test given ante, using a commercial bearing shell faced with the cadmium-silver-copper alloy, the following results were obtained in a 48 hour test run.

Table B

Bearing shell weight	Original oil	Improved lubricant
	Grams	Grams
Before test.....	27.5603	36.3610
After test.....	27.0818	36.3641
Total change.....	−0.4785	+0.0031
Bearing appearance (after test).....	Badly pitted and etched	Good

From the above results, the beneficial effect of the alkyl polysulfides as an improvement agent for the oil is quite apparent. This improved lubricant when tested in an automobile engine equipped with like bearings was highly satisfactory and no deterioration of the bearing was observed after a severe test run. Thus the standard test and actual service test gave similar results.

EXAMPLE 3.—Employing the same motor oil and the mixing procedures as in Example 2, 0.3

per cent by weight of the same amyl polysulfide is incorporated in the motor oil. The improved motor oil so obtained is likewise satisfactory for lubricating these alloy bearings without any substantial deterioration of the metal. When likewise subjected to the standard laboratory test, the following results were obtained.

Table C

Bearing shell weight	Original oil	Improved lubricant
Before test.....	Grams 27.5803	Grams 36.0410
After test.....	27.0818	36.0422
Total change.....	-0.4785	+0.0012
Bearing appearance (after test).....	Badly pitted and etched	Good

The improved motor oil so obtained in addition to inhibiting the destructive action of oil deterioration products on the metal alloy bearings, also has a markedly improved load carrying capacity. The increased extreme pressure properties may be readily measured by means of the Almen testing machine, a standard test method for lubricants required for lubrication under high pressures. The following table gives the results of such a test upon the lubricant obtained in Example 3 as compared with the lubricating base employed.

Table D

Lever load, pounds.....	8-18
Torque, pounds.....	8-18
Weight loadings, lb./sq. in.....	4000-8000

The above results show the ability of these organic polysulfides to impart extreme pressure characteristics to the lubricant.

The above examples are but illustrative embodiments of the present invention and in practice other embodiments may be used. Other di-alkyl polysulfides may be used in lieu of the amyl derivatives employed in these examples and similar improvements obtained. Also, the percentage of di-alkyl polysulfide employed may be varied as indicated according to the particular polysulfide employed and according to the particular properties desired in the final lubricants. Likewise the lubricating base itself may be selected according to the type of final lubricant to be produced. For instance, any of the usual greases or the usual blends of mineral and non-mineral oil may be employed as a lubricating base in making lubricants of those types. The addition of the

alkyl polysulfides to these lubricating bases produces a like improvement in film strength and stability. When incorporating the organic polysulfide in a grease composition or like thickened lubricant, mechanical agitators rather than a current of air are employed to obtain uniform mixing and blending. That is, the polysulfide and grease may be compounded in the usual mixers such as blade mixers, equipped with heating jackets. However, in making such greases the di-alkyl polysulfide may be first incorporated with the oil base according to the procedure of Example 1 and then the metal soap or the thickening agents added to the improved oil, in the ordinary way to produce the desired grease compositions. In other words, the improved mineral oils of the present invention may be used in lieu of the ordinary oils in making special lubricating compositions such as greases, etc.

As stated ante, the incorporation of alkyl polysulfides with the lubricating base produces several improvements in the final lubricant without deleteriously affecting the desirable properties. While the exact reasons for the improvements obtained are not fully known, we are satisfied with observing and utilizing the actual improvements obtained by adding and incorporating these organic polysulfides with commercial lubricants.

What we claim is:

1. A method of lubricating bearing surfaces in internal combustion engines when subjected to conditions of operation which comprises maintaining between bearing surfaces, one of which is an alloy formed chiefly of a metal selected from the class consisting of cadmium and copper, a film of lubricating oil which initially produces an effective lubricating action but which would normally tend to corrode the aforesaid alloy, and maintaining the effectiveness of the lubricating oil by incorporating therein 0.05 to 0.50 per cent of a di-alkyl polysulfide having the following formula



wherein n is 1 or 2, the amount of said di-alkyl polysulfide being sufficient to substantially retard the corrosion.

2. The process of claim 1 wherein said di-alkyl polysulfide is di-amyl polysulfide.

3. The process of claim 1 wherein said di-alkyl polysulfide is di-amyl trisulfide.

4. The process of claim 1 wherein said di-alkyl polysulfide is di-amyl tetra-sulfide.

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