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LUBRICATING COMPOSITION

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This invention relates to lubricating compositions. In one of its aspects, it relates to a lubricating composition comprising a minor amount of a metal dithiocarbamate and a polymer of arylene sulfide. In another of its aspects, the invention relates to a method for improving the lubricating qualities of a natural or synthetic base oil by adding thereto a derivative of a dithiocarbamic acid and a polymer of arylene sulfide. In a further aspect of this invention, the arylene sulfide polymers used are prepared by reacting at least one polyhalo-substituted aromatic compound with an alkali metal sulfide in a polar organic solvent. In a still further aspect of the invention the metallic derivative of dithiocarbamic acid is a molybdenum dithiocarbamate.

Expansion of science and technology has brought new demands on industry for development of lubricants with improved properties. In this space age, for example, it is required that metallic parts coat with one another for extended periods of time under various and sundry conditions of temperature, pressure, and atmosphere. Further, new products require parts to function with minimum wear for extended periods of time without servicing. The automobile industry, for example, has extended the time between servicing of automobiles. Various new lubricants have been developed for these purposes. Some new lubricants generally are produced by adding organic or organometallic compounds to various base oils.

I have now discovered that a composition with unexpected excellent lubricating properties results when minor amounts of a metal dithiocarbamate and a polymer of arylene sulfide are added to a lubricant base. The wear which results from using the combination of the dithiocarbamate and the arylene sulfide polymer is less than that which results from either of these compounds used singularly.

It is an object of this invention to provide a lubricating composition. It is a further object of this invention to improve the lubricating qualities of natural and synthetic base oils. It is a further object of this invention to provide a combination of additives for a lubricating base oil which operate in an unexpectedly beneficial manner. It is a further object of this invention to provide a composition which will decrease the wear on bearing surfaces.

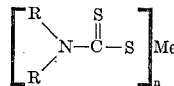
Other aspects, objects, and the several advantages of this invention are apparent from the study of this disclosure and the appended claims.

According to the present invention, the properties of a lubricant can be improved by adding a minor amount of a metal dithiocarbamate and a polymer of arylene sulfide. It has been found that lubricants containing .01 to 10 weight percent of a metal dithiocarbamate and .1 to 50 weight percent of arylene sulfide polymers synergistically exhibit improved lubricating properties particularly when formulated into greases used to reduce wear on metallic surfaces.

The dithiocarbamate compounds which are applicable

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for use in this invention are those which correspond to the following general formula:

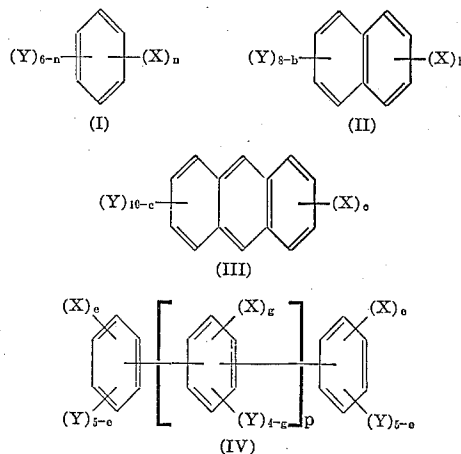


wherein R can be hydrogen or alkyl, cycloalkyl, aryl, aralkyl, or alkaryl radicals having up to 20 carbon atoms and Me can be molybdenum, zinc, lead, cadmium, magnesium, tin, aluminum, and iron, and n is the valence of Me. Some examples are:

- Molybdenum dithiocarbamate
- Molybdenum dimethyldithiocarbamate
- Molybdenum di-*n*-butyldithiocarbamate
- Molybdenum di-*n*-dodecyldithiocarbamate
- Molybdenum dibenzoyldithiocarbamate
- Molybdenum di(4-*tert*-butylphenyl)dithiocarbamate
- Zinc diphenyldithiocarbamate
- Zinc methylethyldithiocarbamate
- Zinc di-*sec*-amyldithiocarbamate
- Lead di-*n*-eicosyldithiocarbamate
- Lead dicyclohexyldithiocarbamate
- Cadmium diethyldithiocarbamate
- Magnesium methylphenyldithiocarbamate
- Tin di-*sec*-butyldithiocarbamate
- Aluminum di(2-ethylhexyl)dithiocarbamate
- Iron di-*n*-hexyldithiocarbamate

The arylene sulfide polymers which are applicable for use in this invention are those prepared by reacting at least one polyhalo-substituted aromatic compound with an alkali metal sulfide. The reaction is preferably carried out in a reaction medium comprising a polar organic compound which is a solvent for the reactants and which is stable at the reaction conditions. *N*-methylpyrrolidone is a preferred reaction medium. The arylene sulfide polymers used in this invention are not the subject of this application per se as they are claimed elsewhere.

The polyhalo-substituted aromatic compounds which can be employed as primary reactants for the preparation of the arylene sulfide polymer are represented by the formulas:



wherein each X is a halogen selected from the group consisting of chlorine, bromine, iodine and fluorine, preferably chlorine and bromine; each Y is selected from the group consisting of hydrogen, and alkyl, cycloalkyl, aryl

radicals and combinations of these containing from 1 to 12 carbon atoms, inclusive; n is an integer of 2 to 6, inclusive; b is an integer of 2 to 8, inclusive; c is an integer of 2 to 10, inclusive; e is an integer of 1 to 5, inclusive; g is an integer of 0 to 4, inclusive; and p is a whole integer selected from the group consisting of 0 and 1.

The compounds of the above general formulas which are preferred are those which contain not more than three halogen atoms and preferably are dihalo-substituted compounds. Some specific examples of the polyhalo-substituted compounds of the above general formulas which can be used in preparing the poly(arylene sulfide) component of the present invention are:

1,2-dichlorobenzene
2,5-dichlorotoluene
1,4-diiodobenzene
1,4-difluorobenzene
1,2,4,5-tetrabromobenzene
1-n-butyl-2,5-dichlorobenzene
1,4-dibromo-2,3,5,6-tetrafluorobenzene
4-chlorobromobenzene
1-cyclohexyl-2,5-diiodobenzene
1-n-dodecyl-2,5-dichlorobenzene
1,3,5-trichloro-2,4,6-triphenylbenzene
1,4-dichloro-7,8-diethylnaphthalene
1,4-dichloroanthracene
4,4'-dichlorobiphenyl
3,3',3''-trichloro-p-terphenyl

and the like.

The alkali metal sulfide reactants for the polymer formation are the monosulfides of sodium, potassium, lithium, rubidium, and cesium. The preferred sulfide reactant is sodium sulfide and its hydrates.

Polar organic solvents applicable as the medium in which the metal sulfide reacts with the polyhalo-substituted compound to form the polymer component of the inventive composition include the classes of amides, lactams, sulfones, and the like. Some examples are:

N-methyl-2-pyrrolidone
Pyrrolidone
Caprolactam
Tetramethylurea
Sulfolane
Dimethylacetamide
Low molecular weight polyamides

and the like.

The combination of the above described organometallic compounds and arylene sulfide polymers can be used with beneficial results in a variety of lubricating compositions. These lubricating compositions may comprise a mineral oil base such as conventionally refined crude oil lubricating stocks having viscosities in the range of 50–1500 SUS (100° F.). In addition to these natural base oils, synthetic base oils may also be used. These latter include polymerized olefins, copolymers of alkylene glycols and oxides, organic esters of polybasic organic and inorganic acids, silicone polymers and the like.

The additives of the present invention have particular application in grease compositions which comprise suitably refined mineral oils thickened by at least one agent such as metallic soaps, high molecular weight olefin polymers, carbon black, finely divided silica and the like.

The usage of a metal dithiocarbamate and an arylene sulfide polymer in the lubricating compositions can vary over a wide range; the amount of metal dithiocarbamate compound can be in the range of about 0.01 to about 10 weight percent, preferably about 0.1 to 4 percent, and the arylene sulfide polymer can be in the range of from about 0.1 to about 50 weight percent, preferably about 0.5 to 10 percent, based on the total lubricant composition. A particularly effective ratio of dithiocarbamate to polymer is 1:1. The remainder of the lubricant composition can comprise the aforementioned base oils and

various other conventional additives such as those normally used as thickeners, antioxidants, VI improvers, pour point depressants, corrosion inhibitors, demulsifiers, detergents, foam inhibitors, and the like.

The lubricant compositions of the present invention are prepared by using conventional techniques. For example, the base oils and other ingredients, including the additives of this invention, are brought together in a mixing vessel. For maximum convenience in mixing and subsequent lubricating effectiveness, the solid ingredients should be in a fine state of subdivision. With constant agitation the mixture is heated and blended at temperatures ranging from 100 to 500° F. for a period of time sufficient to attain maximum homogeneity and effectiveness. The blend is then cooled to room temperature.

The invention can be further illustrated by the following example.

Example

The invention additives were tested in a commercial grease composition (Philube ASM) which consisted of one weight percent high density polyethylene, 9 weight percent lithium 12-hydroxystearate, with the remainder being a 500 SUS (100° F.) conventionally refined neutral oil having a viscosity index of 89. To this base grease were added minor quantities of polyphenylene sulfide (PPS) and a molybdenum dibutylthiocarbamate (Vanderbilt OD 623). The resulting composition was subjected to a wear test in a Shell 4 ball tester.

The polyphenylene sulfide (PPS) was prepared by charging a solution of 1 g. mole of sodium sulfide in 1 liter N-methylpyrrolidone (previously dried by heating at 190° C. in flowing nitrogen) into a 316 SS rocker-bomb together with 1 g. mole p-dichlorobenzene. The bomb and contents were brought to a temperature of 565° F. in about three hours and then maintained at 560–570° F. and at a pressure of about 200 p.s.i.g. for three more hours. The bomb was then cooled, the contents filtered, and the finely divided solid washed repeatedly and alternately with water and methanol. The solid was finally dried at 125° C. under vacuum. Four additional runs were carried out in an essentially identical manner and the finished products were blended. The powdery material had a melting point of 280° C. and an ash content of 0.32 weight percent. Elemental analysis showed 0.71 percent Cl, 28.6 percent S, 3.9 percent H, and 66.5 percent C.

The Shell 4 ball tester is a conventional grease testing device (Precision Scientific Catalog No. 75015) wherein three ½" diameter (52100 steel) balls are fixedly mounted in a cup filled with the test grease (about 10 ml.). A fourth ball is mounted on a rotatable spindle in a position contacting the three fixed balls. The fourth ball is then rotated at 1800 r.p.m. for one minute under a load of 80 kg. After this period the wear on the three fixed balls is microscopically measured, averaged, and reported in terms of microns wear.

The results of the testing are seen in the table below. Prior to evaluation, the additives and the base grease were blended for 30 minutes in a Hobart mixer.

Grease:	Shell 4-ball wear, microns
Philube ASM	2200
Philube ASM 1 wt. percent OD 623 (molybdenum compound)	1860
Philube ASM 1 wt. percent PPS (polyphenylene sulfide)	1500
Philube ASM 0.5 wt. percent OD 623 and 0.5 wt. percent PPS	1040

It can be seen from the above data that less wear occurred when using a combination of the two ingredients than the addition effect of that which occurred when either ingredient was used singularly.

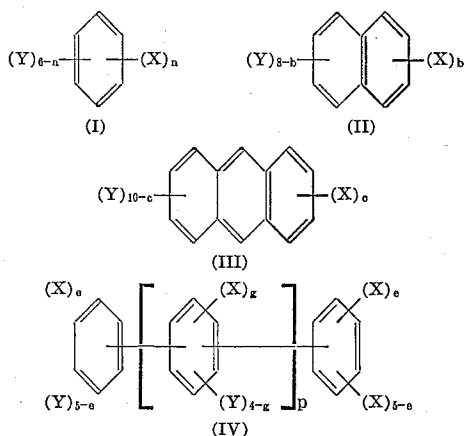
Reasonable variation and modification are possible within the scope of the foregoing disclosure and the appended

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claims to the invention, the essence of which is that minor amounts of a metal dithiocarbamate and a polymer of arylene sulfide are used in a lubricant base to provide an improved lubricant.

I claim:

1. A lubricant composition comprising .01 to 10 weight percent molybdenum dithiocarbamate, 0.1 to 50 weight percent arylene sulfide polymer prepared by reacting an alkali metal sulfide with a polyhalo-substituted aromatic compound selected from the group consisting of compounds of formulas:



wherein each X is a halogen selected from the group consisting of chlorine, bromine, iodine, and fluorine; each Y is selected from the group consisting of hydrogen, and alkyl, cycloalkyl, aryl radicals and combinations of these containing from 1 to 12 carbon atoms, inclusive; n is an integer of 2 to 6, inclusive; b is an integer of 2 to 8, inclusive; c is an integer of 2 to 10, inclusive; e is an integer of 1 to 5, inclusive; g is an integer of 0 to 4,

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inclusive; and p is a whole integer selected from the group consisting of 0 and 1; and a mineral oil having a viscosity in the range of 50–1500 SUS (100° F.).

2. A lubricating composition consisting essentially of a refined neutral oil containing about one weight percent high density polyethylene, 9 weight percent lithium 12-hydroxystearate having a viscosity index of 89, 0.5 weight percent of a polymer prepared by reacting *p*-dichlorobenzene with sodium sulfide in *N*-methylpyrrolidone, and 0.5 weight percent molybdenum dibutyl-dithiocarbamate.

3. A lubricating composition consisting essentially of a refined neutral oil containing about one weight percent high density polyethylene, 9 weight percent lithium 12-hydroxystearate having a viscosity index of 89, 0.5 weight percent of a polymer prepared by reacting an aromatic halide with an alkali metal sulfide in a polar organic solvent, and 0.5 weight percent of molybdenum dithiocarbamate.

4. A lubricating composition according to claim 1 wherein the ratio of said arylene sulfide polymer to said molybdenum dithiocarbamate is 1:1.

5. A lubricating composition according to claim 1 wherein the weight percentage of said arylene sulfide polymer is 0.5 and the weight percentage of said molybdenum dithiocarbamate is 0.5 based on the weight of lubricant.

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