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STABILIZATION OF LUBRICANTS

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This invention relates to the stabilization of lubricants and, more particularly, to the use of improved inhibitors for effecting the stabilization of lubricants.

The advancing technology in the design and development of mechanical equipment employing moving parts is accompanied by the need for improved lubricants to service the moving parts operated at higher speeds, higher temperatures, higher pressures, higher altitudes, longer distances, etc. The lubricant must function at temperatures ranging as low as -65°F. to as high as $400^{\circ}\text{--}500^{\circ}\text{F.}$

One method of meeting these severe requirements is in improvements in the refining and treating of lubricating oils of natural origin. Another method of meeting these requirements is the development of synthetic oils of lubricating viscosity. In both cases, the properties of the oils must be further improved by the addition of additives thereto in order to meet the severe requirements.

The same extreme requirements are encountered in the development of greases which will be suitable for use under the severe conditions hereinbefore set forth. In one method the grease is formulated from an oil of lubricating viscosity. The oil and other components used in the formulation of the grease must be selected to produce the optimum formulation. However, here again, an additive is required in order to produce a final grease which will operate satisfactorily under the severe conditions hereinbefore set forth.

Oils of lubricating viscosity vary considerably in properties, depending upon the chemical composition when synthetically prepared and upon the geographical origin and methods of refining for the naturally occurring oils. Regardless of which oil of lubricating viscosity is employed and which particular formulation is utilized in preparing the grease, it has been found necessary, from a practical consideration, to incorporate an additive therein in order to prepare a final product which will meet the severe requirements.

The severe requirements applied to the lubricant also apply to the additive used in the lubricant. The additive must be very effective in stabilizing the lubricant and, in addition, must possess other improved properties. The additive must be compatible with the lubricant, it must be suitable under the severe conditions of operation and must not contribute any undesirable properties to the lubricant. In addition to all this, the additive must not be excessive in cost which could preclude its commercial acceptance and, also, the additive must be readily available in the required quantities.

Applicant has made an extensive investigation of additives for use in lubricants and has found that certain diaminodiphenyl methane derivatives satisfactorily meet the severe requirements hereinbefore set forth. The diaminodiphenyl derivatives heretofore proposed comprise N,N' -di-sec-alkyldiaminodiphenyl methanes and certain N,N,N',N' -tetra-alkyldiaminodiphenyl methanes. These additives do not contain sulfur and, therefore, cannot cause corrosion which might occur because of the sulfur. These additives have no metallic constituents and, therefore, do not introduce metallic deposits. While these additives are very effective, it has been found that even further improved benefits are obtained when employing a diaminodiphenyl methane derivative containing cyclohexyl substitutions attached to the amino nitrogens.

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The present invention is particularly applicable to the stabilization of greases. In one embodiment the grease is made by compositing an oil of lubricating viscosity, which may be of natural origin or synthetically prepared, with a thickening agent. Metal base greases employ metallic soaps as the thickening agent. These greases are further classified as lithium base grease, sodium base grease, calcium base grease, barium base grease, strontium base grease, aluminum base grease, etc. and mixed base greases including calcium-lithium base grease, lithium-barium base grease, strontium-lithium base grease, etc. These greases are solid or semi-solid gels and, in general, are prepared by the addition to the lubricating oil of hydrocarbon soluble metal soaps or salts of higher fatty acids as, for example, lithium stearate, calcium stearate, calcium acetate, calcium propionate, barium stearate, barium acetate, barium propionate, aluminum naphthenate, etc., or mixtures thereof. The grease also may contain thickening agents such as silica, carbon black, metal oxides, phthalocyanines, polyacrylates, talc, bentonite and organo-treated clays, etc. Alkylureas, arylureas, p-tolyl and p-chlorophenylurea derivatives of bitoylyendiisocyanate, N-n-octadecylterephthalamate and other organic thickeners may be used. Another type of grease is prepared from oxidized petroleum wax, to which the saponifiable base is combined with the proper amount of the desired saponifying agent, and the resultant mixture processed to produce a grease. Other types of greases in which the features of the present invention are used include petroleum grease, whale grease, wool grease, etc., and those made from inedible fats, tallow, butcher's waste, etc.

As hereinbefore set forth, the oils of lubricating viscosity, used as such or in formulating the grease, may be naturally occurring or synthetically prepared. The naturally occurring oils include particularly the petroleum lubricating oils and, more particularly, the more highly refined oils for use under severe operating conditions. The lubricating oils of petroleum origin include those referred to as motor lubricating oil, railroad type lubricating oil, marine oil, transformer oil, turbine oil, transmission oil, differential oil, diesel lubricating oil, gear oil, cutting oil, rolling oil, cylinder oil, hydraulic oil, slushing oil, specialty products oil, etc.

The synthetic lubricating oils are of various types including aliphatic esters, polyalkylene oxides, silicones, esters of phosphoric and silicic acids, highly fluorine-substituted hydrocarbons, etc. Of the aliphatic esters, di-(2-ethylhexyl) sebacate is being used on a comparatively large commercial scale. Other aliphatic esters include dialkyl azelates, dialkyl suberates, dialkyl pimelates, dialkyl adipates, dialkyl glutarates, etc. Specific examples of these esters include dihexyl azelate, di-(2-ethylhexyl) azelate, bis-(1-methyl cyclohexylmethyl) sebacate, di-3,5,5-trimethylhexyl glutarate, di-3,5,5-trimethylpentyl glutarate, di-(2-ethylhexyl) pimelate, di-(2-ethylhexyl) adipate, triamyl tricarballylate, dipropylene glycol dipelargonate, 1,5-pentanediol-di-(2-ethylhexanonate), etc. The polyalkylene oxides include polyisopropylene oxide, polyisopropylene oxide diether, polyisopropylene oxide diester, etc. The silicones include methyl silicone, methylphenyl silicone, chlorophenyl silicone, methylchlorophenyl silicone, etc., and the silicates include, for example, tetraisooctyl silicate, tetrakis-n-dodecyl silane, didodecyl-diethyl silane, diphenyl-di-n-dodecyl silane, octadecyltridecyl silane, hexa-2-ethylhexoxy-disiloxane, etc. The highly fluorinated hydrocarbons include fluorinated oil, perfluorohydrocarbons, etc.

Other synthetic lubricating oils proposed for use in high temperature service as, for example, jet fuel lubrication, include (1) various phosphates as tricresyl phos-

phate, trioctyl phosphate, trinonyl phosphate, tridecyl phosphate, tris-(chlorophenyl) phosphate, chlorophenyl phenyl phosphate, as well as mixed aryl and alkyl phosphates, (2) neopentyl glycol esters, in which the ester group contains from 3 to 12 carbon atoms or more, and particularly neopentyl glycol propionates, neopentyl glycol propionates, neopentyl glycol butyrates, neopentyl glycol caproates, neopentyl glycol caprylates, neopentyl glycol pelargonates, etc., (3) trimethylol alkanes such as trimethylol ethane, trimethylol propane, trimethylol butane, trimethylol pentane, trimethylol hexane, trimethylol heptane, trimethylol octane, trimethylol decane, trimethylol undecane, trimethylol dodecane, etc., as well as the esters thereof and particularly the triesters in which the ester portions each contain from 3 to 12 carbon atoms and may be selected from those hereinbefore specifically set forth in connection with the discussion of the neopentyl glycol esters, and (4) pentaerythritol esters including, for example, pentaerythritol tetracaproate, pentaerythritol tetrapropylate, pentaerythritol tetrapelargonate, pentaerythritol tetravalerate, etc.

In one embodiment the present invention relates to the method of stabilizing a lubricant, which comprises incorporating therein a stabilizing concentration of 4,4'-dicyclohexyldiaminodiphenyl methane.

In a specific embodiment the present invention relates to a method of stabilizing grease, which comprises incorporating therein a stabilizing concentration of 4,4'-dicyclohexyldiaminodiphenyl methane.

In another embodiment the invention relates to a lubricant containing the inhibitor as herein set forth.

As hereinbefore set forth and as will be shown by the examples appended to the present specifications, unexpectedly superior results are obtained in the stabilization of lubricants by incorporating therein 4,4'-dicyclohexyldiaminodiphenyl methane.

In another embodiment of the invention, the 4,4'-dicyclohexyldiaminodiphenyl methane may contain one or more substituents attached to one or both of the phenyl rings and/or to one or both of the cyclohexyl rings. These substituents may be selected from hydrocarbons, including alkyl groups which may contain from 1 to 20 carbon atoms each, generally from 1 to 12 carbon atoms each, and thus are selected from methyl, ethyl, propyl, isopropyl, butyl, sec-butyl, tert-butyl, pentyl, hexyl, cyclohexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, etc.

In another embodiment the substituents comprise alkoxy groups including methoxy, ethoxy, propoxy, isopropoxy, butoxy, tert-butoxy, pentoxy, hexoxy, heptoxy, octoxy, nonoxy, decoxy, etc. In still another embodiment the substituents may contain nitrogen as in amino groups, alkyl amino groups, dialkyl amino groups, amino alkyl groups, dialkyl aminomethylene groups, etc. For certain specific oils, the substituents may comprise a halogen, including particularly chlorine. It is understood that a mixture of the substituents may be employed.

The inhibitor of the present invention is prepared in any suitable manner. Diaminodiphenyl methane may be purchased in the open market or it may be prepared by the reaction of formaldehyde with aniline in the presence of an acidic catalyst, such as hydrochloric acid. The diaminodiphenyl methane then is reductively alkylated with cyclohexanone or a substituted cyclohexanone in the presence of a suitable catalyst to produce the desired inhibitor.

Any suitable catalyst is used in the reductive alkylation including those containing platinum, palladium, cobalt, nickel, molybdenum, etc. Another catalyst used for this reaction is a mixture of the oxides of chromium copper and barium. In general, the reaction is effected at an elevated temperature of from about 200° to about 500° F. and a hydrogen pressure of from about 50 to about 2000 pounds or more per square inch.

In another method the inhibitor is prepared by the reaction of N-cyclohexylaniline with formaldehyde in the presence of an acidic catalyst. For example, 2 moles of

N-cyclohexylaniline and 1 mole of formaldehyde are reacted in the presence of concentrated hydrochloric acid under refluxing conditions. Generally, it is preferred to add the formaldehyde gradually to the refluxing mixture of N-cyclohexylaniline and hydrochloric acid.

The inhibitor is used as an additive in the lubricant in a small but sufficient concentration to obtain the desired stabilization. This concentration may range from about 0.001% to about 25% and, more particularly, from about 0.01% to about 5% by weight of the lubricant. The inhibitor is added to the lubricant in any suitable manner and preferably with intimate mixing in order to obtain uniform distribution of the inhibitor in the lubricant. In some cases the inhibitor may be added to the lubricant during the manufacture thereof as, for example, when used in grease the inhibitor may be added to one or more of the components of the grease before final composing thereof. When desired, the inhibitor may be prepared as a solution in a suitable solvent including, for example, aromatic hydrocarbons such as benzene, toluene, xylene, ethylbenzene, cumene, decalin, etc., or mixtures such as naphtha, kerosene, lube oil, etc.

It is understood that the inhibitor may be used along with other additives incorporated in the lubricant. For example, a metal deactivator, dye, viscosity index improver, pour point depressant, anti-foaming additive, lubricity and extreme pressure additive, anti-scuffing additive, detergent, etc. may be incorporated in the lubricant. These other additives may be selected from zinc dialkyldithiophosphate, zinc dialkyldithiocarbamate, cadmium dialkyldithiocarbamate, phosphorus pentasulfide-olefin reaction products, sulfur-olefin reaction products, sulfurized terpenes, aromatic hydroxysulfides and disulfides and their neutralization products with calcium, barium and magnesium oxides or hydroxides, calcium, barium or magnesium sulfonates, barium or calcium alkylphenates, etc., various high molecular weight amines, alkanolamines, N-alkylalkanolamines, N-alkyl-di-alkanolamines, N¹,N²-dialkyl - polyalkylene-polyamines, N,N'-dialkyl-alkylenediamines, basic high molecular weight β,α -alkylamino amides, β,α -alkylamino esters, glyoxalidines, imidazolidines, imidazolines, etc. It is understood that the other additives will be selected to meet the requirements of the specific lubricant being produced. When desired, the inhibitor of the present invention may be prepared as a mixture with one or more of these other additives and incorporated in this manner in the lubricant.

The following examples are introduced to illustrate further the novelty and utility of the present invention but not with the intention of unduly limiting the same.

Example I

As hereinbefore set forth, 4,4'-dicyclohexyldiaminodiphenyl methane possesses unexpectedly superior properties for use as an additive in lubricants. This is exemplified in the present example in which three different commercial petroleum lubricating oils were used separately in the formulation of lithium base greases. As hereinbefore set forth, the lubricating oils vary considerably in their properties, including their susceptibility to additives.

In the samples utilizing the additive, the additive was added in a concentration of 0.3% by weight of the lubricating oil. Approximately 92% of the lubricating oil then is mixed with approximately 8% by weight of lithium stearate. The mixture is heated to about 450° F., with constant agitation. Subsequently the grease is cooled, while agitating, to approximately 250° F., and then the grease is further cooled slowly to room temperature.

The stability of the grease is tested according to ASTM D-942 method, in which method a sample of the grease is placed in a bomb and maintained at a temperature of 50° F. Oxygen is charged to the bomb and the time required for a drop of 5 pounds' pressure is taken as the induction period.

In all cases reported in the following table, different

preparations of grease were made without an additive, with 4,4'-dicyclohexyldiaminodiphenyl methane and with various other additives as representative of those heretofore proposed for use in lubricants.

Grease A was formulated using a commercial Mid-Continent lubricating oil having an SAE viscosity of 20.

Grease B was formulated using a different commercial Mid-Continent lubricating oil having an SAE viscosity of 20.

Grease C was formulated using a commercial Pennsylvania lubricating oil having an SAE viscosity of 20.

The results of evaluations of the different samples of grease are reported in the following table.

TABLE I

Additive (0.3% by weight)	Induction Period, Hours		
	Grease A	Grease B	Grease C
None	5	8	6
4,4'-dicyclohexyldiaminodiphenyl methane	>360	175	85
4,4'-di-sec-butylidiaminodiphenyl methane	175	53	52
4,4'-tetramethyldiaminodiphenyl methane	9	39	50
Phenothiazine	85	55	34

As hereinbefore set forth, the grease samples were prepared from different commercial lubricating oils. It will be noted that these different greases responded quite differently to the incorporation of the additives.

From the data in the above table, it will be seen that 4,4'-dicyclohexyldiaminodiphenyl methane was outstanding in its potency in stabilizing the grease. This is surprising as compared, for example, to the 4,4'-di-sec-butylidiaminodiphenyl methane which, in itself, is a very potent inhibitor for lubricants.

The high potency of 4,4'-dicyclohexyldiaminodiphenyl methane is also surprising when compared with phenothiazine, which is a well-known inhibitor for lubricants.

Another additive proposed for lubricants is 4,4'-tetramethyldiaminodiphenyl methane. From the data in the above table, it will be seen that this inhibitor is of very low potency in the oils used in the preparation of the greases. As hereinbefore set forth, these oils are commercial products and are representative of those presently being used.

Example II

4,4'-dicyclohexyldiaminodiphenyl methane was evaluated in a synthetic lubricating oil marketed commercially under the trade name of "Plexol 201."

The evaluation was made in accordance with an oxygen stability test, in which a 100 cc. sample of the synthetic lubricating oil is placed in a bath maintained at 400° F. and air is blown therethrough at a rate of 5 liters of air per hour. The sample of synthetic lubricating oil is examined periodically and the time to reach an acid number of 5 is reported. It is apparent that the longer the time required to reach an acid number of 5, the more stable is the lubricating oil. In other words, it takes longer for the more stable oil to deteriorate.

When evaluated in the above manner, a sample of the lubricating oil without additive developed an acid number of 5 (induction period) in 9 hours. In contrast, another sample of the same lubricating oil containing 1% by weight of 4,4'-dicyclohexyldiaminodiphenyl methane did not develop an acid number of 5 until 48 hours. Accordingly, it will be seen that the inhibitor served to stabilize the lubricating oil.

Example III

4,4'-dicyclohexyldiamino-2,5-2',5'-tetramethoxydiphenyl methane was prepared by commingling 120 g. (0.5 mole) of N-cyclohexyl-2,5-dimethoxy aniline with 55 g. of concentrated hydrochloric acid and 110 g. of water.

The mixture was refluxed and 20 g. (0.25 mole) of formaldehyde were added gradually to the mixture undergoing mixing and refluxing. The reaction product then was neutralized with 25 g. of sodium hydroxide in water, dissolved in benzene, washed with water and crystallized from alcohol and n-heptane. The product was recovered as crystals having a melting point of 238°-242° F.

One percent by weight of the additive prepared in the above manner was added to another sample of "Plexol 201" and, when evaluated in the same manner as described in Example II, this served to increase the induction period of the lubricating oil from 9 hours to 33 hours.

Example IV

4,4'-dicyclohexyldiaminodiphenyl methane was prepared by reductively alkylating 4,4'-diaminodiphenyl methane with cyclohexanone at 320° F. in the presence of hydrogen and a catalyst. After crystallization from heptane, the product had a basic molecular weight of 363, which corresponds to the theoretical molecular weight for 4,4'-dicyclohexyldiaminodiphenyl methane of 362.

The inhibitor, as prepared in the above manner, was evaluated in a pentaerythritol ester synthetic lubricant available commercially from Hercules Powder Company as "Hercoflex 600" and is stated to have an acid number of 0.10 maximum, a saponification number of 410, a refractive index at 20° C. of 1.453 and a specific gravity at 25/25° C. of 0.997.

The evaluations in the pentaerythritol ester were made in substantially the same manner as described in Example II for dioctyl sebacate. The inhibitor was used in a concentration of about 1% by weight of the lubricating oil.

When evaluated in this manner, a sample of the pentaerythritol ester without inhibitor, reached an acid number of 5 within 16 hours. In contrast, the sample of pentaerythritol ester containing about 1% by weight of 4,4'-dicyclohexyldiaminodiphenyl methane did not reach an acid number of 5 until 73 hours.

Example V

Another synthetic lubricating oil consists of esters of trimethylolpropane. A lubricating oil available commercially comprises trimethylolpropane esters having an average molecular weight of about 457 and the ester portions have an average of 7 carbon atoms each. Typical properties of such a lubricating oil, available commercially from the Celanese Corporation of America under the trade name of "Cellutherm," are set forth below:

Specific gravity, 60/60° F.	0.965
Acidity, mg./KOH/g.	0.03
Color, ASTM	2
Fire point, COC, ° F.	520
Flash point, COC, ° F.	460
Hydrolysis number	0.27
Viscosity:	
At -65° F., cs.	14,900
At 100° F., SSU	76.93
At 210° F., SSU	37.77

One percent by weight of 4,4'-dicyclohexyldiaminodiphenyl methane is incorporated in a sample of the synthetic lubricating oil described above and this serves to improve stabilization of the lubricating oil during use.

Example VI

A calcium base grease is prepared using dioctyl sebacate ("Plexol 201") as the lubricating oil. One percent by weight of the inhibitor is incorporated in the dioctyl sebacate and then the mixture is commingled with calcium stearate in a proportion of 91 parts by weight of the dioctyl sebacate-inhibitor mixture and 9 parts by weight of calcium stearate. The mixture is agitated and heated to about 250° F. and then is allowed to cool gradually to room temperature. The stability of the grease is eval-

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uated in substantially the same manner as described in Example I.

I claim as my invention:

1. Lubricant selected from the group consisting of grease and oil of lubricating viscosity containing, as an inhibitor against oxidative deterioration, a stabilizing concentration of a 4,4'-dicyclohexyldiaminodiphenyl methane. 5
2. Grease subject to oxidative deterioration containing, as an inhibitor against said deterioration, a stabilizing concentration of 4,4'-dicyclohexyldiaminodiphenyl methane. 10
3. Lubricating oil subject to oxidative deterioration containing, as an inhibitor against said deterioration, a

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stabilizing concentration of 4,4'-dicyclohexyldiaminodiphenyl methane.

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