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LUBRICANT COMPOSITIONS CONTAINING 9-AMINO ACRIDINES

Donald W. Schmulling, St. Louis, Mo., assignor to Shell Oil Company, a corporation of Delaware

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This invention is directed to improved lubricants. More particularly it is directed to the stabilization of such lubricants for use at elevated temperature and under oxidizing conditions.

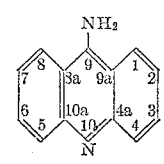
Active development is proceeding in the field of synthetic lubricants for the production of compositions having improved stability required by increasing operating temperatures, both of lubricants, such as oils, greases and hydraulic fluids. Stability, particularly where metals are in contact with the ester, is a complex problem which is concerned not only with the attack upon metal by decomposition products of the ester, but also is concerned as much with changes in the physical properties of the esters. The esters decompose at high temperatures, due either to thermal degradation or to oxidation. Numerous stabilizing substances have been investigated to minimize or counteract the various phenomena encountered during use of aliphatic esters at elevated temperatures. Many of these are effective at relatively mild operating temperatures, but as the temperatures are increased beyond about 350° F., and particularly in the range of 400° F. and above, stabilizers found to be effective at lower temperatures rapidly lose their stabilizing effect and in numerous instances actually become prooxidants.

The resistance of a composition to oxidation or thermal degradation is complicated by the properties of degradation or oxidation products. It is necessary for engine cleanliness for the decomposition products to be as soluble as possible in the lubricating medium. It is also necessary for the stabilizing material to have a sufficiently high boiling point so that it does not evaporate from the composition under the conditions of the high temperature operation. Furthermore, peripheral effects must be minimized insofar as possible. Some stabilizing materials which may be satisfactory insofar as their stabilizing capacity is concerned become of little value due to their physiological effects which become apparent to operators of machines being lubricated by stabilized lubricants, such as by skin irritation or by irritation of eyes and mucous membranes.

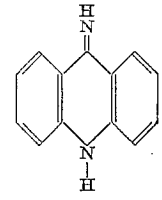
It is an object of the present invention to improve the stability of aliphatic polyesters for use at elevated temperatures. It is a particular object of the invention to improve the stability of aliphatic tetraesters. It is a further object of the invention to improve the stability of greases prepared from stabilized esters. It is another object of the invention to provide stable gas turbine lubricants showing a minimum tendency to increase in viscosity and acid number during use at elevated temperatures. Other objects will be apparent from the description of the invention.

Now, in accordance with the present invention, it has been found that lubricants, especially aliphatic polyesters, can be stabilized, particularly with respect to decomposition at temperatures above 350° F., by the presence of stabilizing proportions of 9-aminoacridines. The restricted class of N-naphthyl-9-aminoacridines comprises novel compounds having unique properties of imparting outstanding oxidation resistance to lubricants, especially aliphatic polyester lubricants. More particularly, the invention in its preferred aspect comprises the stabilization of pentaerythritol esters (including dipentaerythritol esters) with 9-aminoacridines, and especially with 9-arylaminoacridines. The chief aspects of this class of stabilizing materials, in addition to the stabilizing effectiveness, comprise their lack of adverse physiological side effects upon operators and the solubility of their by-products in polyesters, thus materially reducing sludging and lacquering.

The stabilizing materials to be utilized in accordance with this invention may be referred to either as 9-aminoacridines or as the tautomeric form thereof, namely, 9-iminoacridan, the latter being favored, although the precise configuration is still in some dispute. For the purpose of the present description, reference will be made throughout to the 9-aminoacridine configuration, although it will be understood that the corresponding acridan formulation is considered to be its equivalent for the present purpose. These two structures may be generalized as follows:



9-aminoacridine



9-iminoacridan

The 9-aminoacridines to be used in these compositions are preferably either those in which the amino group in the 9 position is unsubstituted or bears aryl or alkyl radicals. Preferably, the amino group in the 9 position bears either hydrogen or one aryl or alkyl substituent, the dialkylamino acridines being less effective. The preferred subgeneric class comprises the 9-arylamino acridines of which the 9-naphthylamino acridines (especially N-β-naphthyl-9-aminoacridine) are most effective in the lubricants, especially aliphatic polyester compositions. The following list includes typical 9-aminoacridines which may be utilized for the described purpose.

The aminoacridines having more than one amino radical have limited solubility in some of the esters. Their effectiveness is not decreased thereby, especially in environments where solubility is not a problem, as in greases. The derivatives bearing substituents having hydrogen atoms bonded to secondary or tertiary carbon atoms are less effective than those species having no alkyl substituents other than methyl radicals.

The acridine nucleus may be modified by the presence of substituents other than hydrogen including amino radicals in other than the 9 position as well as alkyl or aryl substituents. As the intended temperatures of use of the compositions increase, it is preferred to increase the molecular weight of the 9-aminoacridine compound, either by increasing the molecular substituent weight of the 9-amino grouping or by substituting on other parts of the acridine nucleus either alkyl or aryl substituents.

9-AMINOACRIDINES

9-aminoacridine
9-phenylaminoacridine
9-α-naphthylaminoacridine
9-β-naphthylaminoacridine
1,9-diaminoacridine
2,9-diaminoacridine
3,9-diaminoacridine
4,9-diaminoacridine
2,7,9-triaminoacridine
9-tolylaminoacridine
9-xylylaminoacridine
1-methyl-9-phenylaminoacridine
2-ethyl-9-(β-naphthylamino)acridine
3-isopropyl-9(α-naphthylamino)acridine
4-phenyl-9-isopropylaminoacridine
N-phenanthryl-9-aminoacridine
1-amino-9-phenylaminoacridine
1,9-diphenylaminoacridine
2-amino-9-α-naphthylaminoacridine
2,9-di(β-naphthylamino)acridine
3-amino-9-tolylaminoacridine
3,9-di(tolylamino)acridine
4-amino-9-α-naphthylaminoacridine
4,9-di(xylylamino)acridine
9-methylaminoacridine
9-isopropylaminoacridine
9-tert-butylaminoacridine
9-hexylaminoacridine
9-(phenylmethylamino)acridine
9-benzylaminoacridine

The 9-amino acridines may be utilized in the aliphatic polyesters in proportions varying from about 0.1 to about 5% by weight of the total composition. Preferably they are utilized in amounts from about 0.5 to 4% by weight thereof. The actual proportion employed may vary with the molar concentration, the preferred molar concentration being between about 0.01 and 0.15, subject in part to solubility of the compound in the specific aliphatic polyester.

Lubricants which may be stabilized with the aminoacridines include mineral oils, olefin, polymers, polyoxyalkylene compounds, and especially, aliphatic polyesters.

The aliphatic polyesters which may be utilized as the lubricating fluids are preferably tetraesters, such as the pentaerythritol esters or the dimers or trimers of the same. Preferably, each radical contains from 4 to 18 carbon atoms each and preferably from 6 to 14 carbon atoms each. Typical species include pentaerythritol tetracaproate, pentaerythritol tetravalerate, pentaerythritol tetraheptoate, pentaerythritol dicaproate divalerate, pentaerythritol tricaproate heptoate and mixtures thereof. It will be noted that the esters may be either mixed esters or mixtures of homo esters, the best rheological properties being obtained with mixed esters. For use at elevated temperatures the dipentaerythritol esters are preferred due to their greater molecular weight and consequently higher boiling points.

Aliphatic diesters may be utilized in place of or in addition to the tetra or hexa esters of pentaerythritol or its dimer.

As diesters there may be used one or more of the compounds of the formula ROOC—Z—COOR wherein Z is an alkylene chain of four to eight carbon atoms and R is an alkyl group of four to fourteen carbon atoms, being the residue of an aliphatic monohydric alcohol from butyl to tetradecyl alcohols. Dicarboxylic acids which provide the above esters are adipic, pimelic, suberic, azelaic, and sebacic. The alcohols include butyl, isobutyl, or sec-butyl alcohols and the various amyl, hexyl, octyl, nonyl, decyl, undecyl, dodecyl, and tetradecyl alcohols. The alcohols with branched hydrocarbon chains provide diesters with particularly desirable properties. Typical of these are isobutyl, 2-ethylbutyl, 2-ethylhexyl,

1-methylhexyl, 1-methylheptyl, 1-methyl-4-ethyloctyl, 2,2,4-trimethylhexyl, 2-isopropyl-3,3-dimethylbutyl, 1,4-dimethylbutyl, and 1-isobutyl-4-ethyloctyl alcohols.

ESTER LUBRICANTS

Bis(2-ethylhexyl) sebacate
Bis(isononyl) sebacate
Bis(2-ethylhexyl) adipate
Bis(1-methylheptyl) azelate
Bis(2,2,4-trimethylhexyl) pimelate
Bis(1,4-diethylhexyl) adipate
Bis(1,4-dimethyloctyl) adipate
Bis(2-ethylbutyl) suberate
2-ethylhexyl isononyl sebacate
1-methylhexyl 2-ethylbutyl sebacate

In addition to the types of esters described above, fluorinated esters may be utilized. Such esters include those formed between dicarboxylic acids and fluorine-containing alcohols or glycols, esters of glycols with fluorine-containing acids and other types of fluorine containing esters.

Other types of esters susceptible to inhibition as described comprise esters of polyaikylol alkanes, such as 1,1,1-trimethylolethane, bis(2-hydroxymethyl)propane, 1,1,2-trimethylolpropane, 1,1,2,2-tetramethylolethane, and others, preferably esterified mixtures of fatty acids having 4 to 12 carbon atoms per molecule.

Another type of ester includes those formed between aliphatic dicarboxylic acids having 4–20 carbon atoms per molecule and monoethers of polyoxyalkylene glycols. A specific example is the sebacic acid ester of the 2-ethylhexanol ether of propylene oxide and ethylene oxide copolymers.

The compositions comprising aliphatic polyesters and 9-aminoacridines may be utilized without further modification or may be converted into other lubricating compositions such as greases. Gelling agents which are useful include the conventional soaps such as alkali metal (e.g., sodium, lithium), alkaline earth metal (e.g., calcium), polyvalent metal (e.g., aluminum, lead) and other soaps of fatty acids (stearic acid) or of hydroxy fatty acids (12-hydroxystearic), especially where temperatures do not exceed about 300° F. For higher temperatures, it is advisable to utilize grease-forming colloids such as silica aerogels, finely divided silica prepared by burning silanes, clays, ammonium clays such as trimethyl stearyl ammonium bentonites and especially high temperature gelling agents such as indanthrene dyes, indogens and polymer coated clays such as clays coated with phenol-formaldehyde resins, aniline-formaldehyde resins and the like. Graphite may be employed for this purpose as well. The proportion of gelling agent will depend upon the consistency of the grease desired and upon the temperatures to which the grease compositions will be subjected. Normally, this will be between about 2 and 40% by weight of the total grease composition. Methods of preparing such greases are known in the art.

In order to demonstrate the advantages of this invention, tests were conducted to demonstrate the oxidation stability of the compositions at high temperatures. These tests were conducted at a temperature of 400° F., one liter of air per hour being bubbled through the sample of 20 grams in the presence of copper, silver, iron and magnesium catalyst washers. Table I summarizes the data obtained during these tests. The additives were dissolved in pentaerythritol tetracaproate. From the table it will be seen that acridine resulted in a composition having relatively short life. Moreover, at the test temperature acridine gave off fumes which were irritating to both the skin and mucuous membranes. An advantage was gained by combination of the 9-aminoacridines with a thiodiarylamine, such as phenothiazine, a diarylamine (such as diphenylamine or dinaphthylamine) or with combinations of the same.

Table I

HIGH TEMPERATURE OXIDATION TESTS OF ACRIDINE DERIVATIVES IN PENTAERYTHRITOL TETRACAPROATE

[5 liter air per hour/per 100 g. sample. Catalysts (Cu, Ag, Fe, Mg)]

	Molar conc.	Percent weight conc.	Hours tested	Hrs. to absorb 1 Millimole O_2/g.	Induction period	Acid number	Percent visc. increase 100° F.	Benz. insoluble	Temp., ° F.	CU corrosion mg./cm.[3]
INHIBITORS										
9-amino acridine	.026	.50	66	65	56	5.0	25	.09	400	None
9-aniline acridine	.019	.50	45	45	31	5.2	29	.04	400	None
N-α-naphthyl-9-amino acridine	.016	.50	46	45	31	5.2	33	.04	400	None
N-β-naphthyl-9-amino acridine	.016	.50	49	49	36	5.1	22	.03	400	None
9-anilino acridine	.025	.50	67	67	58	2.7	25	Trace	400	None
N-α-naphthyl-9-amino acridine	.025	.80	80	80	66	3.7	27	.12	400	None
N-β-naphthyl-9-amino acridine	.025	.80	83	83	72	2.3	21.4	Trace	400	+0.52
9-amino acridine	.050	.97	118	118	115				400	+1.02
N-β-naphthyl-9-amino acridine	.050	1.60	146	146	146				400	
COMBINATIONS										
9-amino acridine +phenothiazine	[1].025		101	101	None				400	None
9-amino acridine+2,2′-dipyridylamine	[1].025		131	131	None				400	−0.68

[1] Each.

The stability of compositions within the invention was studied at 450° F. for 72 hours while bubbling 1 liter per hour of air per 20 grams sample through the composition, coupons of metals being suspended in the sample. Table II gives the data obtained. The base fluid was pentaerythritol esters of a mixture of C_{6-12} fatty acids and contained the additives noted.

The N-naphthyl-9-aminoacridines may be prepared, for example, by heating 9-chloroacridine with a (α- or β-)-naphthylamine, preferably the primary amine. This class has remarkably outstanding stabilizing properties, as compared with other known oxidation inhibitors, especially in aliphatic polyesters and particularly in pentaerythritol esters.

Table II

HIGH TEMPERATURE OXIDATION TEST ON PENTAERYTHRITOL TETRACAPROATE CONTAINING VARIOUS INHIBITORS

Inhibitors and concentration, percent weight	Hours for oxidation rate to reach		Total mmole O_2 absorb./g. sample after 72 hr. oxid.	CU corr. mg./cm.[2]	Properties of oxidized sample		
	0.85 millimole/hr.	1.1 millimole/hr.			acid number	percent visc. increase	percent weight benzene insolubles
1.6% N-β-naphthyl-9-aminoacridine	22	29	3.67	+.50	8.9	141	.17
2.4% N-β-napthyl-9-aminoacridine	34	48	2.80	+.42	6.2	79	.23
4.0% N-β-naphthyl-9-aminoacridine	39	71	2.61	+1.76			
1% β,β-dinaphthylamine plus 1.6% N-β-naphthyl-9-aminoacridine	27	38	3.00	+.56	7.9	117	.58
5% phenothiazine plus 1.6% N-β-naphthyl-9-aminoacridine	33	49	3.00	+.44	6.7		1.26
1% β,β-dinaphthylamine plus 0.5% phenothiazine plus 0.8% N-β-naphthyl-9-aminoacridine	28	65	2.91	+.32	7.9	102	.96
1% β,β-dinaphthylamine plus 0.5% phenothiazine plus 1.6% N-β-naphthyl-9-aminoacridine	49	>72	2.56	+.66	7.0	96	.51
1% β,β-dinaphthylamine plus 0.5% phenothiazine plus 2.4% N-β-naphthyl-9-aminoacridine	41	>72	2.86	+1.28			
1% β,β-dinaphthylamine plus 0.5% phenothiazine plus 3% N-β-naphthyl-9-aminoacridine	33	>72	2.80	+1.32			
1% diphenylamine plus 0.5% phenothiazine plus 1.6% N-β-naphthyl-9-aminoacridine	35	>72	3.08	+.48	6.6	142	1.10
1% diphenylamine plus 0.25% 2,2-diphenylamine plus 1.6% N-β-naphthyl-9-aminoacridine	28	41	2.95	+.62	7.3	97	.77

The effectiveness of aminoacridines in other types of esters, such as esters of polyalkylolalkanes, is demonstrated by the data contained in Table III. The base fluid was an ester of 1,1,1-trimethylolethane, the esterifying acids being n-butyric (15%), n-caproic (45%) and n-caprylic (40%).

Table III

400°F./72 HOUR OXIDATION-CORROSION TEST

Test results	1% weight β,β′ dinaphthylamine, 0.5% weight phenothiazine, 1.6% weight N-β-naphthyl-9-aminoacridine, 96.9% weight ester
Weight change of metal specimens (mg./cm.[2]):	
Copper	+0.18.
Magnesium	+0.16.
Silver	+0.20.
Steel	+0.15.
Aluminum	+0.13.
Percent viscosity increase of oxidized ester at 100° F.	20.0.
Acid number of oxidized ester (mg. KOH/g.)	0.5.
Visual sludge rating	Medium.

I claim as my invention:

1. A lubricating composition comprising a major proportion of an aliphatic polyester lubricant and a minor proportion, sufficient to improve the oxidation resistance of the lubricant of a 9-aminoacridine selected from the group consisting of 9-aminoacridine, a 9-(N-arylamino)-acridine, a 9-(N-phenylamino)acridine, and a 9-(N-beta-naphthylamino)acridine.

2. A lubricating composition comprising a major proportion of an aliphatic polyester lubricant and a minor proportion, sufficient to improve the oxidation resistance of the aliphatic polyester lubricant, of 9-aminoacridine.

3. A lubricating composition comprising a major proportion of an aliphatic diester lubricant and a minor proportion, sufficient to improve the oxidation resistance of the ester, of a 9-(N-arylamino)acridine.

4. A lubricating composition comprising a major proportion of an aliphatic tetraester lubricant and a minor proportion, sufficient to improve the oxidation resistance of the ester, of a 9-(N-arylamino)acridine.

5. A lubricating composition comprising a major proportion of an aliphatic pentaerythritol ester lubricant and

a minor proportion, sufficient to improve the oxidation resistance of the ester of a 9-(N-arylamino)acridine.

6. A lubricating composition comprising a major proportion of an aliphatic pentaerythritol ester lubricant and a minor proportion, sufficient to improve the oxidation resistance of the ester, of 9-aminoacridine.

7. A lubricating composition comprising a major proportion of an aliphatic pentaerythritol ester lubricant and a minor proportion, sufficient to improve the oxidation resistance of the ester, of 9-(N-phenylamino)acridine.

8. A lubricating composition comprising a major proportion of an aliphatic pentaerylthritol ester lubricant and a minor proportion, sufficient to improve the oxidation resistance of the ester of 9-(N-β-naphthylamino)acridine.

9. A lubricating composition comprising a major proportion of an aliphatic pentaerythritol ester of fatty acids having 4–18 carbon atoms per molecule and a minor proportion, sufficient to improve the oxidation resistance of the ester, of a 9-(N-arylamino)acridine.

10. A lubricating composition comprising a major proportion of an aliphatic pentaerythritol ester of fatty acids having 6–14 carbon atoms per molecule and a minor proportion, sufficient to improve the oxidation resistance of the ester of 9-(N-β-naphthylamino)acridine.

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