

UNITED STATES PATENT OFFICE

2,354,252

LUBRICATING COMPOSITION

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No Drawing. Application February 11, 1941,
Serial No. 378,444

1 Claim. (Cl. 252—51)

The present invention is directed to the treatment of lubricating oils and lubricant compositions to reduce the formation of sludge and of corrosive-forming acids during the time the lubricating oil or composition is used in the combustion engine cylinder. With the increase of high pressures in the combustion cylinder, the amount of sludge derived from the lubricating oil or composition has greatly increased and, therefore, it has become of great importance to devise a remedy to inhibit the production of sludge. When lubricating oils or lubricant compositions containing mineral oils are subjected to the conditions prevailing in the cylinders of internal combustion engines, deterioration occurs due to thermal action and oxidation in the presence of a diversity of metals which may be in a massive state or in a finely divided state, or in both. This deterioration is due to the formation of carbonaceous and coke-like materials and a variety of oxygenated products as well as degradation, interaction, condensation, polymerization, dehydrogenation, and dehydration products. Such action is evidenced by impairment of color of the lubricating material, carbon formation, sludge formation, acid formation, and/or viscosity increase. The relative extent of each action varies with the type of the lubricating oil or composition and the process used in producing and refining said lubricating oil or composition.

Further, various materials added to the oil for specific purposes, as for example, detergents for Diesel lubrication, or various extreme pressure additives, may greatly affect the extent of each action. More specifically, in modern engines, due to the high pressure and high operating temperature, it has been ascertained that it is desirable to replace the hitherto-used babbitt bearings with other alloy bearings such as cadmium, silver-cadmium, nickel or copper-lead. In other words, the babbitt bearings have been found to wear and deteriorate in tensile strength, and have therefore been replaced to a substantial extent by new bearing alloys. These new bearing alloys are rather sensitive to the acids formed in the lubricating material, oil or composition, said acids functioning to corrode the bearings. Stated differently, lubricating materials such as mineral oils or mineral oil compositions which have not been inhibited relative to oxidation exert a corrosive action on the bearings.

It has also been ascertained that some of the alloy constituents of the new bearing alloys function as oxidation catalysts, that is, function to promote the formation of acids and sludge in the mineral oil. Therefore, it becomes necessary

from this standpoint to inhibit the formation of sludge and acids in the lubricating oil.

In accordance with the present invention, lubricating mineral oils and lubricating compositions containing mineral oils are stabilized against oxidation under conditions prevailing during combustion in the engine cylinder of an internal combustion engine by having present in the lubricant a small amount of a phenylene diamine. The addition of said phenylene diamine improves the stability of the composition towards the action of oxygen or oxygen bearing gases at elevated temperatures, either in the presence of metals, metal compounds, or soluble metal salts generally present in the operating cylinders of internal combustion engines.

The present invention is particularly applicable to petroleum hydrocarbons and especially to representative oils from Pennsylvania, the Mid-Continent, and to Gulf Coastal crudes. Solvent treated oils and compositions containing the same, and petroleum hydrocarbons with additive ingredients, may also be treated in accordance with the present invention, and the so-treated oils are stable towards oxidation. There may be present in the lubricating oil or composition pour point depressors, viscosity index improvers, detergents, extreme pressure additives, oiliness additives, phosphite esters, and other organic phosphorous compounds, sulfurized fixed oils, anti-corrosives, metal poisoners, and other oxidation inhibitors.

It has been discovered that the phenylene diamines are soluble in lubricating petroleum hydrocarbons and mineral oil in amounts varying between .01 to .1% based on the weight of the hydrocarbon material treated, and further, it has been found that these small amounts are sufficient to inhibit against oxidation. More specifically, it has been discovered that the addition of .03 to .05% of the phenylene diamines based on the weight of the lubricating oil represents the optimum amounts for the stabilization of most lubricating oils. It has also been ascertained that certain oils may be beneficially stabilized by having more than .1% of the phenylene diamines present. The discovery has been made that it is not only the phenylene diamine which goes into solution which is effective to promote and achieve stabilization, but that undissolved phenylene diamine dispersed through the lubricating oil or composition also effects stabilization. More specifically, up to 1% of phenylene diamine in dispersion, in some cases, promotes stabilization.

It has also been discovered that the phenylene diamines not only function as anti-oxidant and anti-sludge forming agents, but also the phenylene diamines do not to any material extent affect the viscosity of the so-treated oil. This may be due to the fact that the phenylene diamine prevents the formation of oxidation products in the oil or composition being treated. It may be stated that it is highly desirable to maintain the original viscosity of the lubricating oil or composition which is being inhibited against oxidation and the formation of sludge.

It has also been discovered that the anti-oxidation capacity of certain well-known inhibitors of lubricating oil may be considerably improved by mixing said agents with a small proportion of phenylene diamine, as for example .03 to .05% and, in some cases, up to .1%. In other cases, the phenylene diamine may be mixed with other inhibitors in an amount up to 1%. For example, there may be added to the lubricating mineral oil a mixture of para-amino-phenol and anthranilic acid and any of the phenylene diamines to produce a composite inhibitor of oxidation and a preventative for sludge formation. More specifically, the mineral oil may contain 0.5% of para-amino-phenol, .05% of any of the phenylene diamines, and .1% of anthranilic acid. In the alternative, there may be added to the mineral oil a mixture of .05% of para-amino-phenol and .05% of any of the phenylene diamines. Or there may be added to the mineral oil .1% of anthranilic acid and .05% of any of the phenylene diamines. While these are the preferred percentages, the latter may be considerably varied.

In the more specific aspect of the present invention, it has been ascertained that when heavy metal organic salts have been added to lubricating oils to impart detergent characteristics thereof, the usual undesirable catalytic effect thereof on the oxidation of the lubricating oil can be inhibited by adding a small quantity of a phenylene diamine as, for example .03 to .05% or even .1% or up to 1%. The phenylene diamines are single ring compounds having a benzene nucleus to which are attached two amine groups. The ortho, meta, and para compounds are known and any of these compounds or mixtures of any thereof may be used in carrying out the present invention. The meta and para compounds have been found to be in general more effective than the ortho, but the choice of the particular member of the phenylene diamine group is governed by the nature of the base oil, the additives which may be present therein, and to some extent by the physical characteristics of the phenylene diamines themselves. O-phenylene diamine is a colorless solid melting at 140° C., and boiling at 252° C.; m-phenylene diamine is a colorless solid melting at 63° C. and boiling at 287° C.; p-phenylene diamine is a colorless solid melting at 140° C. and boiling at 267° C. All of these phenylene-diamines are sparingly soluble in the petroleum oils or hydrocarbons herein set forth. The meta and para phenylene diamines are usually preferred in carrying out the present invention in view of the fact that they boil at higher temperatures. The preference is governed not so much by superiority of the meta compound in stabilization, but rather by the physical properties of the meta as compared to the para. The meta has a melting point as shown above of 63° C. as compared to 140° C. for the para, while having also a boiling point of 287° C. as compared

to a boiling point of 267° C. for the para. This lower melting point obviates the possibility of formation of solid crystals by portions of the material driven from the oil at higher temperatures, a contingency which the higher melting point of p-phenylenediamine might occasion. The lower melting point and higher boiling point of m-phenylene diamine also facilitate incorporation and retention of the compound.

The results obtained by adding phenylene diamine to lubricating oils are set forth in the following tables. In the experiments, the results of which are tabulated in said tables, the oxidation resistance of the oil was determined by bubbling oxygen through samples of oil at controlled temperatures in the presence of metallic copper. Copper was used since it is actively catalytic for and is the most generally used catalyst for oxidation of lubricating oils. Viscosity determinations on the oil were made before and after blowing. Neutralization numbers and naphtha insolubles were determined at intervals during and at the completion of blowing. Specifically: 400 c. c. of the oil under test was placed in a glass test tube 50 x 450 mm. The tube was immersed in an oil bath at 300° F. to a depth such that the bath level was well above the surface of the oil under test. 18' of freshly polished No. 14 gauge copper wire, wound in a helix of 40 mm. diameter, was placed in the tube and commercial quality oxygen was admitted thru a 6 mm. glass tube extending to 1/4" from the bottom. An oxygen flow of 10 liters per hour was maintained by the use of a needle valve and flow-meter in the line from the oxygen storage cylinder.

A 50 c. c. sample was withdrawn at 24 hours without interrupting blowing and the entire sample was withdrawn at 48 hours.

The neutralization number set forth in the following tables represents the milligrams of potassium hydroxide necessary to neutralize one gram of oil, and was determined on the sample withdrawn at 24 hours, and on the oil after 48 hours. This determination was made in accordance with the method developed by Fenske, Stevenson et al., and reported in a paper read before the Petroleum Division of the American Chemical Society, Detroit, 1940. The neutralization number was determined in each case in the following manner: 5 grams of the oil was dissolved in 50 c. c. of half and half benzene-butanol mixture, fluorescein and methyl red solutions were added as indicator, and the solution was titrated in a dark room with sodium butylate to a fluorescent endpoint, illuminating from the side with a point source of light.

The naphtha insolubles or sludge shown in the following tables represents milligrams of sludge per 10 grams of oil and was determined by diluting 10 grams of the oil with 100 c. c. of A. S. T. M. precipitation naphtha, shaking and allowing the resulting solution to settle for three hours. The precipitate was collected on an asbestos mat in a Gooch crucible, dried at 300° F. and weighed.

In order to ascertain the effect of the phenylene diamine upon various petroleum hydrocarbon stocks, the following experiments were carried out and the results thereof appear in Table I.

A neutral oil of 200 second Saybolt viscosity at 100° F. from Mid-Continent crude, a bright stock of 120 seconds Saybolt viscosity at 210° F. from Mid-Continent crude and blends of the two to give an S. A. E. 30 paraffin oil were oxidized under the test conditions, without additives and with specified proportions of phenylene diamines.

The phenylenediamines used were of commercial quality, currently available, and the proportion of the other isomers in each was not determined. As shown in Table I concentrations as low as .01% were very effective, while 1%, representing

hours; the neutralization number for the twenty-four hour period and for the forty-eight hour period, and the percentage of viscosity increase at 210° F. Saybolt Universal after a forty-eight

Table I

Oil	Additive	Mg sludge		Neutralization number		Per cent viscosity increase at 210° F. 48 hr.
		24 hr.	48 hr.	24 hr.	48 hr.	
Paraffin neutral S. U. V. 47 at 210° F.	None	65	194	.36	3.2	4
Do.	.05% m-phenylenediamine	6	8	.07	.14	0
Paraffin Bright Stk S. U. V. 121 at 210° F.	None	7	74	3.2	6.5	45
Do.	.05% m-phenylenediamine	4	5	.14	.58	6
Paraffin S. A. E. 30	None	59	121	2.0	3.2	16
Do.	.01% m-phenylenediamine	3	35	.34	.93	2
Do.	.03% m-phenylenediamine	4	8	.24	.41	0
Do.	.05% m-phenylenediamine	6	8	.07	.21	0
Do.	.10% m-phenylenediamine	5	8	.07	.20	0
Do.	1.0% m-phenylenediamine	11	15	.07	.07	0
Do.	.03% o-phenylenediamine	3	11	.14	.50	3
Do.	.05% o-phenylenediamine	3	10	.21	.36	1.5
Do.	.10% o-phenylenediamine	5	11	.29	.46	2
Do.	.03% p-phenylenediamine	3	3	.07	.14	0
Do.	.05% p-phenylenediamine	4	5	.07	.14	.5
Do.	.10% p-phenylenediamine	6	8	.07	.14	.3

a saturated solution with the balance dispersed in finely divided form, was remarkably effective. When treated with .03% or more of phenylene diamine, the oil left no appreciable lacquer on the walls of the glass tube or on the copper wire, whereas the uninhibited oil left a thin brown layer over the entire wall surface and on the copper. In these tests the ortho compound was somewhat less effective than the meta or para compounds.

25 In another experiment, Gulf Coastal and solvent treated Mid-Continent oils were subjected to test without additives and with specified proportions of m-phenylenediamine. The additive was beneficial in all cases. Lacquer formation, 30 conspicuous with the untreated oils, was so reduced as to be scarcely detectable, while sludge formation, acid formation, and viscosity increase were greatly reduced. The results of these experiments are set forth in Table II which follows:

Table II

Oil	Additive	Mg sludge		Neutralization number		Per cent viscosity increase at 210° F. 48 hr.
		24 hr.	48 hr.	24 hr.	48 hr.	
Pennsylvania S. A. E. 30	None	57	93	2.9	4.7	16
Do.	.05% m-phenylenediamine	10	14	.14	.50	0
Gulf Coastal S. A. E. 30	None	90	163	1.0	1.7	12
Do.	.05% m-phenylenediamine	26	62	.36	.36	2
Solvent treated S. A. E. 30 from Mid-Continent fields	None	47	201	2.5	5.6	16
Do.	.05% m-phenylenediamine	19	45	.22	1.7	4

In the following tables there is set forth the particular kind of mineral oil used with and without certain anti-oxidants; the amount of sludge produced in twenty-four hours and forty-eight

In another series of experiments the phenylene diamines were added to oils containing several commonly used additives. The particulars thereof appear in Table III.

Table III

Oil	Additive	Metal catalyst	Mg sludge		Neutralization number		Per cent viscosity increase at 210° F. 48 hr.
			24 hr.	48 hr.	24 hr.	48 hr.	
Paraffin S. A. E. 30+E. P. Diesel additive	None	Cu	36	100	1.7	2.5	10
Do.	.05% m-phenylenediamine	Cu	9	10	.07	.29	0
Gulf Coastal S. A. E. 30+E. P. Diesel additive	None	Cu	221	380	3.4	5.3	45
Do.	.05% m-phenylenediamine	Cu	25	61	.33	.57	5
Paraffin S. A. E. 30+.05% nickel salt of hydrogenated abietic acid	None	Cu	68	133	2.5	4.3	14
Do.	.05% m-phenylenediamine	Cu	8	11	.07	.36	.7
Paraffin S. A. E. 30+.1% phosphite type additive	None	Cu	1	25	.28	1.0	5
Do.	.05% m-phenylenediamine	Cu	6	7	.10	.51	.6
Paraffin S. A. E. 30+.5% tri-m-cresylphosphite	None	Cu	14	13	.26	.36	3
Do.	.05% m-phenylenediamine	Cu	10	9	.17	.36	3
Paraffin S. A. E. 30+.5% paraflow	None	Cu	45	105	2.0	2.7	16
Do.	.05% m-phenylenediamine	Cu	6	7	.09	.17	7
Paraffin S. A. E. 30+.2% paratone	None	Cu	46	98	1.9	2.7	16
Do.	.05% m-phenylenediamine	Cu	7	7	.07	.22	3
Paraffin S. A. E. 30+.2% sulfurized sperm oil	None	Cu	21	73	.87	2.4	10
Do.	.05% m-phenylenediamine	Cu	21	42	.50	.72	4
Paraffin S. A. E. 30+.1% Alox No. 350	None	Cu	59	115	2.0	3.3	13
Do.	.05% m-phenylenediamine	Cu	22	37	.39	.64	3
Paraffin S. A. E. 30+.1% anthranilic acid	None	Cu	3	9	.22	.40	4
Do.	.05% m-phenylenediamine	Cu	4	5	.07	.22	1
Paraffin S. A. E. 30+.05% p-aminophenol	None	Cu	4	17	.22	.58	5
Do.	.05% m-phenylenediamine	Cu	-----	8	.11	.27	1

While the combination was not as effective for oxidation inhibition in some cases as was the phenylene diamine alone, the phenylene diamine addition did not deleteriously affect the composition and was very beneficial in most cases.

The most commercially important pour point depressors are those produced by chlorinating waxy hydrocarbons and then condensing the chlorinated wax either alone or with an aromatic material in the presence of a catalytic agent such as aluminum chloride or other Friedel-Crafts type condensing agent such as zinc chloride or ferric chloride. As an example of this type of compound, Paraflow, a product of the Standard Oil Co., was added to an S. A. E. paraffin oil, and the composition tested with and without added phenylene diamine. The present invention may be carried out using other pour point depressors as, for example, the synthetic oil produced by a low temperature aluminum chloride condensation of chlorinated paraffin wax and naphthalene.

During recent years, certain types of high molecular weight polymeric linear chain compounds have been effectively used to raise the viscosity index of mineral oils. For example, high molecular weight hydrocarbons obtained by polymerizing iso-olefines may be added to lubricating oils with the result that the temperature-viscosity curve of the oil is found in many cases to be remarkably flattened. For example, polymerized isobutylene has been found very useful in raising the viscosity index of lubricating mineral oils. When 100 parts of liquid isobutylene is treated with $\frac{1}{10}$ part of boron fluoride, the isobutylene being cooled by a bath of carbon dioxide at 80° below zero C., polymerization of the isobutylene occurs, the reaction product having a mean molecular weight of 3500. As an example of this popular type of additive, mention may be made of Paratone which is a product manufactured by the Standard Oil Development Co. Paratone was added to an S. A. E. paraffin oil, and the composition tested with and without phenylene diamine.

Chlorinated organic compounds have been widely used as additives to impart high film strength characteristics to lubricating mineral oils. Some of these compounds have the added property of imparting detergency and oiliness characteristics to the composition. For example, there may be incorporated with a mineral oil base chlorinated ring compounds, as for example mono-chlorobenzene or chlorobenzene, chlornaphthalenes, chlordiniphenyls and the like. Further, certain oxygen containing organic ring compounds which have been chlorinated have been found useful for "thin-film" lubricating purposes. Many of these compounds are manufactured by the Lubrizol Sales Corp. Anglamol 714, a product of the Lubrizol Sales Corp. was added to an S. A. E. 30 paraffin oil, and the composition tested both with and without phenylene diamine. Anglamol 714 was also added to an S. A. E. 30 Pale Coastal oil and the composition tested both with and without added phenylene diamine.

Sulfurized animal and vegetable oils have been

widely used as additives to impart film strength and/or anticorrosive properties to lubricant compositions. As an example of this class, a sulfurized sperm oil containing 10% by weight of sulfur in combination was added to an S. A. E. 30 paraffin oil and the composition tested with and without added phenylene diamine.

Aryl and alkyl phosphite esters have been widely used as additives to impart anticorrosive, E. P., or antioxidant properties to the composition. As an example of this type tri-m-cresylphosphite was added to an S. A. E. 30 paraffin oil and the composition tested with and without added phenylene diamine.

Heavy metal salts have been extensively used to impart detergent qualities to oil for Diesel lubrication. Many of these salts are capable of furnishing the necessary detergency but have undesirable catalytic effect on oxidation of the oil to which they are added. As an example of this type of compound the nickel salt of hydrogenated abietic acid was added to an S. A. E. 30 paraffin oil and the composition tested with and without added phenylene diamine.

As stated, the phenylene diamines are soluble in lubricating mineral oils in an amount varying between .01 to .1% based on the weight of the mineral oil treated. When the amount of phenylene diamine is greater than the above, it is desirable, if not necessary, to disperse the phenylene diamine in the mineral oil. Any suitable dispersion agent may be used, but it has been found that alcohol, the ethanolamines, and particularly tri-ethanolamine and butyl carbitol function very satisfactorily as dispersion agents.

It has been found that when a composite anti-oxidant and anti-sludge forming medium is added to the lubricating mineral oil which already contains other anti-oxidants and anti-sludge forming agents, the phenylene diamine functions to increase the activity of the primary anti-oxidant and anti-sludge forming agent.

Referring to Table III, the expression "Alox No. 350" defines the methyl ester of the material consisting mainly of fatty, hydroxy, keto and keto hydroxy acid, together with some unsaponifiable alcohol and alcohol ketone. This compound is made by controlled oxidation of a fraction of Pennsylvania petroleum, and the acids formed range from those containing 5 carbon atoms to 35 carbon atoms.

What we claim is:

A lubricating composition stabilized against oxidation under temperature conditions prevailing during combustion in the engine cylinder of an internal combustion engine, said composition containing as its principal lubricating constituent a major portion of a mineral lubricating oil having incorporated therein an anti-oxidant and anti-sludge forming agent, comprising a primary phenylene diamine, and an ethanolamine acting as a dispersion agent for the phenylene diamine.

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