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LUBRICANT

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This invention relates to the problem of inhibiting bearing corrosion and oil deterioration in internal combustion engines, and is more particularly directed to the use of a particular class of compounds as inhibitors in conjunction with mineral lubricating oils for the lubrication of moving parts of an internal combustion engine.

In recent years alloys such as cadmium-silver, cadmium-silver-copper, cadmium-nickel-copper and copper-lead have been substituted for babbitt as bearing metals. Although these alloys have mechanical advantages over Babbitt metal, under modern operating conditions they appear to promote oxidation of the lubricating oil, resulting in varnish and sludge formation with attendant valve and ring sticking. The use of these bearings also is attended with high bearing losses, probably due to corrosion by acids formed by the oxidation of the oil.

Because of the rapid rate of deterioration of lubricating oils and the rapid rate of corrosion of bearings in modern internal combustion engines of the automotive type much research has been conducted on the problem of inhibiting deterioration and corrosion, and a large number of compounds have been developed which are effective to some extent in inhibiting deterioration of the oil and corrosion of the bearings.

We have discovered a class of compounds which exhibit exceptional ability to inhibit deterioration of motor oil and corrosion of bearings when used in relatively small quantities.

An object of this invention is to inhibit deterioration of motor oil and to inhibit corrosion of bearings in internal combustion engines.

A further object of the invention is to provide a composition of matter capable of lubricating internal combustion engines containing bearings of the afore-mentioned type without causing excessive corrosion thereof.

Still another object of the invention is to inhibit varnish and sludge formation in internal combustion engines.

Another object of the invention is to provide a lubricant for lubricating internal combustion engines which is resistant to oxidation and deterioration during use.

Further objects of this invention will appear from the following description.

In accordance with our invention we provide means for contacting the bearings and other moving parts of the internal combustion engine with an ester or salt of a thio-carbamic acid, in the presence of mineral lubricating oil. Although the salt or ester of the thio-carbamic acid may be injected into the engine independently of the lubricating oil, we prefer to mix the material in small quantities with the lubricating oil prior to adding it to the engine. Although it is not essential that the salt or ester be soluble in the oil, we prefer to use a soluble material in order to insure against separation of the material from the oil during use. The invention, however, contemplates the use of salts or esters which are not soluble but which are highly dispersed in and held in suspension in the oil. As examples of compounds which are suitable may be mentioned alkyl, aryl and aralkyl esters of mono-thio-carbamic, di thio carbamic, and thio phospho carbamic acids in which hydrogen in the amino group in either unsubstituted or substituted by aryl, alkyl, or aralkyl radicals. Specific compounds which may be mentioned as examples are benzyl dibutyl dithio carbamate and the butyl ester of dibutyl dithio carbamic acid. As examples of salts may be mentioned the alkaline earth metal salts including barium, calcium, strontium and magnesium of mono-thio-carbamic, di-thio-carbamic and thio-phospho carbamic acids.

Although the aforesaid esters and salts are effective when added to lubricating oil in amounts as low as .25% by weight and amounts greater than 5% by weight, the preferable range is from .5 to 5% by weight based on the mineral oil.

In order to demonstrate the efficacy of the thio carbamic acid esters and salts as inhibitors against bearing corrosion and motor oil deterioration, Underwood tests were made using various amounts of benzyl dibutyl dithio carbamate and butyl ester of dibutyl dithio carbamate acid in mineral lubricating oil and the results obtained were compared with results obtained on the motor oil without any additive. The results are given in the following table. The lubricating oil used in all tests was a Pennsylvania neutral oil having a viscosity of 180 seconds Saybolt at 100° F. The Underwood test is described in an article entitled "Automotive bearing materials and their applications," by

A. F. Underwood, Journal of Society of Automotive Engineers, volume 43, pages 385–392, September 1938.

A catalyst consisting of .12% iron naphthenate by weight was added to the oil in each run. This percentage is equivalent to .01% iron as iron oxide. The use of an iron catalyst is standard practice for the Underwood test.

Table

Per cent by wt. additive	0	5	3	1	0.5	5	3
Additive No	None	#1	#1	#1	#1	#2	#2
Hours run	10	10	10	10	10	10	10
CuPb loss grams	.1626	.0198	.0176	.0318	.0380	.2536	.2607
AgCd loss do	1.1258	.0041	.0030	.0045	.0071	.0044	.0097
Neutralization No	13.95	0.59	0.61	1.40	1.63	1.40	1.10
Per cent naph. insol	2.99	0.36	0.42	0.45	0.61	0.22	0.93
Per cent $CHCl_3$ sol	2.88	0.21	0.22	0.29	0.29	0.17	0.62
Per cent sol. sludge	8.35	0.23	0.20	0.87	1.49	0.46	0.40
Per cent S. in blend from additive	0	1.085	.651	.217	.1085	1.225	.735

Additive #2=butyl ester dibutyl dithio carbamic acid.
Additive #1=benzyl dibutyl dithio carbamate.

The data opposite the headings Per cent naph. insol., Per cent $CHCl_3$ sol., and Per cent sol. sludge were obtained in the following manner:

Naphtha insoluble (insoluble sludge)

Three grams of the oil is mixed in an Erlenmeyer flask with 100 cc. of A. S. T. M. precipitation naphtha, of the type specified in A. S. T. M. Method D91–35. The oil and naphtha are thoroughly mixed and allowed to stand for three hours. The insoluble matter is then filtered through a tared Gooch porcelain crucible, previously prepared with an asbestos pad 1'' thick and dried in an oven at 300° F. for 30 minutes. The insoluble residue is washed with 100 cc. A. S. T. M. naphtha and dried in an oven at 300° F. for thirty minutes, cooled and weighed. The increase in weight is "naphtha insoluble."

Chloroform soluble

The chloroform soluble is extracted from the dried and weighed "naphtha insoluble" residue by pouring successive portions of chloroform through the filter pad using light suction. 100 cc. of chloroform is generally sufficient but the extraction should be continued until the filtrate is colorless. (With heavy "naphtha insoluble" residues the chloroform is allowed to stand in the crucible without suction for a few minutes before each portion of the chloroform is drawn through the crucible.)

The residue is then dried in an oven at 300° F. for 30 minutes, cooled and weighed. The loss in weight is "chloroform soluble."

The solubility in chloroform of the residue from the "naphtha insoluble" determination is affected by the time and temperature of drying. For this reason, in order to secure check results in the "chloroform soluble" determination, the drying time and temperature, especially in the "naphtha insoluble" determination, should be carefully controlled.

It usually happens that in the Underwood test there is no particular difficulty in filtering, regardless of whether the oils contain detergents or not. However, when these methods are applied to used crankcase oils it sometimes happens that oils which contain detergents will not give a clear filtrate. Under these conditions, the filtrate is refiltered through a second Gooch filter and the deposits from both crucibles added in reporting naphtha insoluble (and chloroform soluble).

Propane insoluble (soluble sludge)

The filtrate from the naphtha insoluble is concentrated to 20 cc. by evaporation and is transferred quantitatively to the extraction apparatus described in Industrial & Engineering Chemistry April 15, 1939, page 183. The remaining naphtha is now completely removed from the oil sample by evaporation on a steam bath. The propane extraction is carried out as directed in the above-mentioned article. The propane insoluble material remaining is calculated in percentage and reported as soluble sludge.

The data in the tables show that benzyl dibutyl di thio carbamate was effective in amounts of from .5 to 5% in cutting down bearing loss in both copper lead and silver cadmium bearings and that it was effective in these percentages in improving the neutralization number, the per cent naphtha insoluble, the per cent chloroform soluble, and the per cent soluble sludge. The results further show that with respect to this particular additive the addition of 5% showed no material benefit over the addition of 3% to the motor oil.

The table shows that when butyl ester of dibutyl thio carbamic acid was used as the additive the copper-lead bearing loss was worse than when no additive was used, but in all other respects the oil was markedly superior to the oil without the additive. The results on this particular additive also demonstrate that in general the effectiveness of the 5% additive was greater than 3%

From the foregoing it is apparent that we have discovered a new class of inhibitors for preventing deterioration of motor oils when used in internal combustion engines and for inhibiting bearing corrosion in such engines and that we have discovered a new type of lubricant which is unusually stable under operating conditions in internal combustion engines and which gives efficient operation of the engine because of the small amount of acid, sludge and varnish formed.

We claim:

1. A lubricant for internal combustion engines comprising a mineral lubricating oil and a small amount, sufficient to inhibit oxidation of said oil in use, of benzyl dibutyl dithio carbamate.

2. A lubricant in accordance with claim 1 in which the amount of benzyl dibutyl dithio carbamate is from 0.5 to 5% by weight of the mineral oil.

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