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LUBRICANTS CONTAINING CERTAIN ORGANO-LEAD NITROGEN COMPOUNDS

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U.S. Cl. 252—49.7

32 Claims

ABSTRACT OF THE DISCLOSURE

Organolead nitrogen compounds in which the lead is tetravalent and is attached to carbon and to nitrogen, and in particular to lubricants containing such compounds effective as antiwear additives for lubricants. In many instances such utility is enhanced by incorporating certain antioxidants. A method of preparation is also described wherein trialkyllead hydroxide is reacted with the desired heterocyclic compound in an organic solvent with the formation of water and the desired organolead nitrogen compound.

This application is a continuation-in-part of application Ser. No. 665,969, filed Sept. 7, 1967, now abandoned which is a continuation of application Ser. No. 601,321, filed Dec. 13, 1966, now abandoned.

The present invention relates to organolead nitrogen compounds in which the lead atom is tetravalent and is joined directly to carbon and to nitrogen, and to lubricants containing the same.

An object of the invention is to obtain such organolead compounds which are useful as additives for lubricating oils and greases.

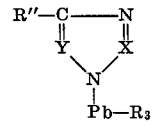
Still another object is to devise additives which will greatly enhance the lubricating properties of oils and greases, and the anti-wear properties of oils and greases.

A further object is to provide auxiliary compounds in the nature of antioxidants which will be compatible with the lead compounds and will substantially increase the lubricating effectiveness thereof.

In general, the compounds which meet the objects set forth above are represented by names or formulas as follows:

(a) Trialkylplumbyl cyanamide and trialkylplumbyl cyanoguanidine in which the alkyl group has 1 to 12 carbon atoms;

(b)



wherein

X=N, CH or CR'

Y=CH, CØ, CR, or N when X is CH or CR'

R=alkyl of 1 to 12 carbon atoms

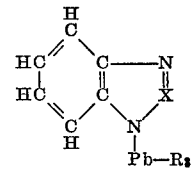
R'=phenyl and alkyl of 1 to 20 carbon atoms

R''=H, NH_2, NHR''', alkyl having 1 to 4 carbon atoms, or phenyl

R'''=phenyl or alkyl having 1 to 20 carbon atoms

Ø=phenyl

(c)



wherein X and R have the meaning defined above under (b), but the total number of carbon atoms included in the group R and R' is at least 8.

Examples of the new organolead compounds are given in Table I.

TABLE I

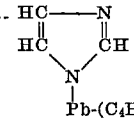
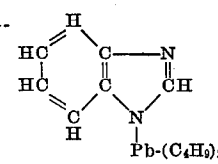
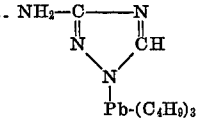
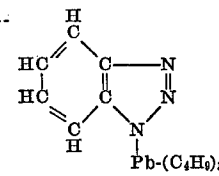
Number:	Name	Formula
1	(Trimethylplumbyl)cyanamide	$(CH_3)_3PbNHCN$
2	N-(tributylplumbyl)imidazole	
3	N-(tributylplumbyl)benzimidazole	
4	3-amino-N-(tributylplumbyl)-1,2,4-triazole	
5	N-(tributylplumbyl)benzotriazole	

TABLE I.—Continued

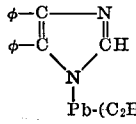
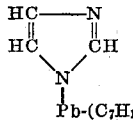
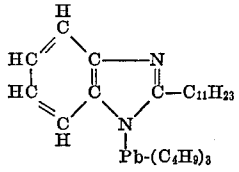
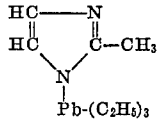
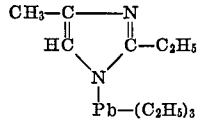
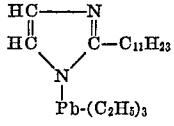
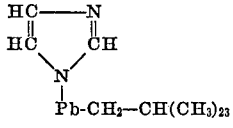
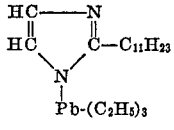
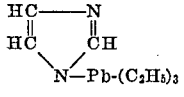
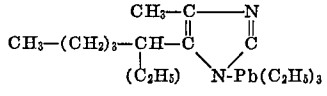
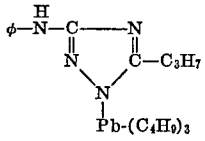
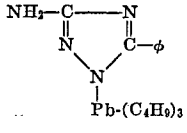
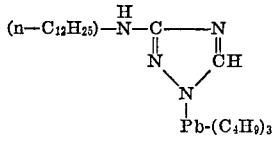
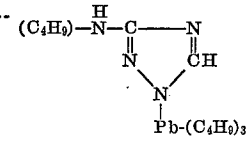
	Name	Formula
6	N-(triethylplumbyl)-4,5-diphenylimidazole	
7	N-(triheptylplumbyl)imidazole	
8	N-(tributylplumbyl)-2-undecylbenzimidazole	
9	N-(triethylplumbyl)-2-methylimidazole	
10	N-(triethylplumbyl)-2-ethyl-4-methyl imidazole	
11	N-(triethylplumbyl)-2-undecyl imidazole	
12	N-(triisobutylplumbyl)imidazole	
13	N-(triethylplumbyl)-2-(branched chain) undecylimidazole	
14	N-(triethylplumbyl)imidazole	
15	N-(triethylplumbyl)-4-methyl-5(1-ethylpentyl)imidazole	
16	N-(tributylplumbyl)cyanoguanidine	
17	3-anilino-5-isopropyl-N-(tributylplumbyl)-1,2,4-triazole	
18	3-amino-5-phenyl-N-(tributylplumbyl)-1,2,4-triazole	
19	3-(n-dodecylamino)-N-tributylplumbyl)-1,2,4-triazole	

TABLE I—Continued

	Name	Formula
20	3-(n-butylamino)-N-(tributylplumbyl)-1,2,4-triazole	
21	N-(triethylplumbyl)cyanoguanidine	
22	N-(tri-n-butylplumbyl)cyanoguanidine	

PREPARATION OF COMPOUNDS 17–20

These compounds may be prepared by mixing tributyllead hydroxide with a desired 1,2,4-triazole in an organic solvent, followed by recrystallization from ethanol. A more detailed description of the preparation is found below in the discussion of the preparation of compounds 2–14.

In addition to the foregoing, there may be mentioned (tributylplumbyl)cyanamide, (tridodecylplumbyl)cyanamide, (trimethylplumbyl)cyanoguanidine, (tridodecylplumbyl)cyanoguanidine, N-(tributylplumbyl)-2-eicosyl imidazole and N-(tributylplumbyl)-4-butyl imidazole. In the above formulas, the alkyl groups are normal unless otherwise indicated. However, any branched chain alkyl of the same number of carbon atoms may be substituted. Furthermore, in order to provide solubility of the compounds in lubricating oils and greases, it is desirable that the total number of carbon atoms in the alkyl and phenyl groups attached to the imidazole or triazole ring should not be greater than 35, and preferably not greater than 20.

Following are descriptions of the methods for preparing the compounds identified above.

PREPARATION OF COMPOUND 1

Trimethyllead cyanamide was prepared by adding an equimolar amount of cyanamide to trimethyllead hydroxide in ethanol. Upon concentrating the solution, the compound crystallized.

PREPARATION OF THE CYCLIC COMPOUNDS, SUCH AS COMPOUNDS 2–14, INCLUSIVE

A triorganolead hydroxide is mixed with the desired heterocyclic compound (which are available in the market) in an organic solvent, followed by recrystallization from ethanol.

Thus in preparing N-(tributylplumbyl)imidazole (compound No. 2) an ethereal tributyllead bromide solution (prepared from 1 mole of lead dichloride) was stirred with excess of silver oxide (from 100 g. of silver nitrate) until bromide-free (ca. 30 min.). The precipitate of silver bromide was separated by filtration and to the remaining solution there was added 34.4 g. of imidazole (0.507 mole) with stirring to dissolve the imidazole and the whole was evaporated to dryness. The residue after solidifying was recrystallized from 500 ml. of 96% by weight ethanol to give 210 g. of N-(tributylplumbyl)imidazole (93% yield based on the hydroxide, 71% based on lead dichloride).

PREPARATION OF COMPOUNDS 16, 21 AND 22

A mixture of 20 g. (0.05 mole) of tributyllead hydroxide and 4.2 g. (0.05 mole) of cyanoguanidine in 350 ml. of ether was stirred at room temperature for three hours. The white, insoluble solid appeared to reach an irreducible minimum, and solid anhydrous sodium sulfate was added. The mixture was stirred an additional 0.5 hour, then filtered. The filtrate was stirippped of volatiles under vacuum. The residue was 20.3 g. of yellow viscous oil.

Analysis.—Calcd. for $C_{14}H_{30}N_4Pb$: Pb, 44.9%. Found: Pb, 45.7% (by flame photometer) and 46.4% (by X-ray fluoresence).

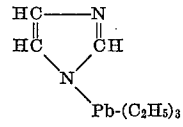
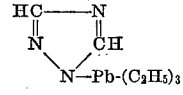
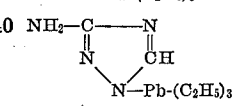
Infrared analysis confirmed the proposed structure of compound 16.

Compounds 21 and 22 are prepared in the same manner as compound 16 above, except that triethyllead hydroxide and triheptyllead hydroxide respectively are employed in place of tributyllead hydroxide.

The preparation of the above-mentioned cyanoguanidine compounds is further described in a copending application by Worrel, filed on Dec. 13, 1966, Ser. No. 601,347, now U.S. Pat. No. 3,436,414 dated Apr. 1, 1969.

In the following table, there are listed the physical properties and analyses of some of the compounds of the invention.

TABLE II

Compound	M.P. or decomposition temp., ° C.		Analyses percent Found	Calcd.
	D.T. 100±1	N Pb	7.49 57.06	7.75 57.32
(No. 2, Table I)	M.P. 48–50	N	6.20	6.29
(No. 12, Table I)	M.P. 167	Pb	46.49	46.50
		N	11.83	11.60
	M.P. 178–181	N	15.52	14.84
(No. 4, Table I)	M.P. 116–118	N Pb	12.45 44.83	12.14 44.89
(No. 3, Table I)	M.P. 104–105	C H	45.70 6.37	46.04 6.51
(No. 5, Table I)	M.P. 103	N Pb	9.04 42.07	8.46 41.72
(No. 1, Table I)	D.T. 126–127	N Pb	9.71 70.82	9.55 70.64
$(C_4H_9)_3PbNHCN$	Oil	N Pb	6.34 49.60	6.68 49.38

The above compounds have been found to be highly valuable as additives to lubricating oils particularly hydrocarbon oils for the purpose of preventing abrasive wear and scuffing or seizure under boundary lubrication conditions. They may also be used with similar effect in hydrocarbon base greases, such as greases thickened with lithium 12-hydroxystearate.

Illustrative examples of hydrocarbon oils to which may be added the novel compounds herein disclosed are naphthenic base stock, paraffinic base stock or a mixture thereof. Such oils are often known as the West Coast crude, the Pennsylvania stock, or the Mid-Continent stock. The novel organolead compounds may also be added to synthetic polyester oils which are esters of polycarboxylic acids such as sebacic acid, adipic acid, azelaic acid, and the like, synthetic polybutene lubricants which are formed from the polymerization of isobutene, and other synthetic lubricants such as polyalkylene glycols, tetrahydrofuran polymer oils, phosphate esters, aromatic ethers, and the like.

While the compounds of the invention are valuable lubricating oil additives per se, their action is enhanced to a considerable degree by the addition of a phenolic type of antioxidant, e.g. the herein designated antioxidant A, to be more fully identified hereinafter. In par-

ticular, the action of the antioxidant is in many cases to increase the wear value of the lubricating oil at a higher temperature, e.g., 125° C. It also has the beneficial effect of increasing the solubility of the lead nitrogen compounds of the invention, thus enabling compounds that are otherwise too sparingly soluble in the oil to be used.

The principal tests indicating the value of additives for the purposes above mentioned were conducted in the Shell 4-Ball Wear Tester, a well-known device, the details of which may be had from the description thereof contained in Lubricating Engineering, vol. 1, p. 35, 1945. In this device, a one-half inch metal ball is rotated under a specified load against three similar balls clamped together in an equilateral triangle. These balls are contained in a heated cup filled with the lubricant. The bulk temperature of the lubricant is measured by a thermocouple inserted in a thermowell in the cup. Torque on the lower ball holder is a measure of the frictional resistance at the rubbing surfaces, and is continuously measured by means of a strain gauge and recorder. The rubbing of the upper ball in the presence of the lubricant against the lower three produces circular concave scars on the lower balls.

With no wear, the balls will have a minimum scar diameter (Hertz diameter) which is the result of plastic deformation of the balls, and is determined by the modulus of elasticity of the material and the load applied. After a wear run, the three scars are measured to 0.01 mm. under a microscope, and the average diameter of the scars is a measure of the wear, and the basis for computation of the unit pressure.

The pressure in the contact zone of balls in the 4-Ball Test decreases greatly during the course of the test, since the load remains constant, while the wear scar area supporting it, increases. For example, with a 15 kg. load on AISI 521000 steel balls, the scar diameter is approximately 0.22 mm., which corresponds to a pressure of 230,000 lbs./in.^{2}. When the scar diameter reaches 0.5 mm., the pressure has dropped to 45,000 lbs./in.^{2}.

One type of 4-Ball Test is designed to measure resistance to abrasive wear. In this test, the bulk lubricant temperature is held at 50° C. or at 125° C., the rotational speed is 1800 r.p.m., and the load is 15 kg. The test is continued, with periodic interruption for measurement, until the average scar diameter has increased to 0.47 mm., corresponding to zone pressure of 50,000 p.s.i. The time required to reach this scar diameter is designated as the "wear time." Effective antiwear additives may increase the wear time from 11–18 minutes to 100 minutes or more.

Tests of the above named compounds carried out in the 4-Ball Tester in mineral oil as above described are shown in Table III. The mineral oil used is a commercial product (Humble Oil Co.) designated by Bayol 85, a highly-refined paraffinic white oil of viscosity 17 centistokes at 100° F., which is widely used in lubrication studies. A solution or finely-divided suspension of the additive was used in an amount sufficient to provide 1% by weight of lead in the oil.

TABLE III.—PROPERTIES OF DIFFERENT ANTIWEAR COMPOUNDS

1	2	3	4	5	6	7
	Color reaction in oil with antioxidant A[1]	Oil solubility[2]		Wear time in minutes		
		No antioxidant	With antioxidant A	In clear oil[3]		In oil and antioxidant 125° C
				50° C.	125° C.	
Additive:						
None				18	11	
1	No	Low	Low	3,000+	120	800–2,400
2	Yes	High	High	3,000+	170	3,000+
3	Yes			3,000+	90	
4	Yes			3,000+	150	
5	No			2,500 est.	39	
7	Yes		High	3,000+		600
8	Yes		do	3,000+		35
10	Yes	Med	Med	3,000+	100	70
11	Yes	High	High	3,000+	150	[4] 900+
12	Yes	Low	Low	3,000+	150	K.
14	Yes	Low	Low	3,000+	100	
15 (0.1% Pb)	Yes	High	High	3,000+		
16	Yes	Low	Low	3,000+	220	
17	Yes	Med	High	900+	130	
18	Yes	Low		900+	240	

[1] Antioxidant A is 4,4'-methylenebis(2,6-di-tert-butylphenol). It was used in the concentration of from 0.5 to 1.0 weight percent of oil. In general, color reaction with antioxidant A is indicative of favorable action of the antioxidant in conjunction with the additive in the 125° C. test.

[2] The solubilities of additives 3, 4, and 5 were not determined but are believed to be low. Columns 3 and 4 give solubilities with and without antioxidant added. In general, "low" means a solubility of 0.1 percent or less by weight of the oil; "med." (medium) means 0.5 weight percent; and "high" means over 1.0 weight percent.

[3] In the tests of additives 4 and 8, the oil contained 0.6 weight percent of antioxidant A.

[4] The test was terminated at 900 minutes and had no evidence of wear.

As will be evident, solubility of the additive in the oil is an important factor in determining its suitability. A number of compounds which have a structure which should enable them to qualify as additives turn out to have too low solubility. In some instances, the additives show up better in the wear-time tests than their solubility would warrant. The explanation is that in these tests, the additive in suspension is effective. Therefore, for practical utilization, the solubility factor must be taken into consideration along with the wear-time factor.

The effect of pre-heating the mineral oil-additive solution was ascertained by heating such mixture for two hours at 125° C. in the test cup of the 4-Ball Tester before starting the wear test at that temperature. In the case of compound 4, such preheating raised the wear time at 125° C. from 150 minutes to in excess of 1560 minutes.

While antioxidant A improved the action of the additives at 125° C., it did not, of itself, show any antiwear activity. Thus, when present in an amount of 0.5 wt. percent of the oil, the wear-time was substantially the same as indicated for the clear oil alone in the first line of the above table.

Tests of additive compound 2 dissolved in mineral oil at varying concentrations are described in Table IV. These tests are carried out in the same manner as described for Table III. The amount of compound 2 tested is sufficient to provide a solution of the additive at the given percentage of lead.

TABLE IV.—ANTIWEAR TESTS OF COMPOUND 2

Percent lead	Percent anti-oxidant	Temperature, ° C.	Wear time, minutes
0	0	50	18
0.01	0	50	730
0.01	0.01	50	675
0.02	0	50	1,950
0.02	0.05	50	1,720
0.10	0	50	3,000+
0	0	125	11
0.5	0	125	71
0.5	0.5	125	450
0.5	1.0	125	3,000+
1.0	0	125	170
1.0	0.5	125	1,120
1.0	1.0	125	3,000+
2.3	0	125	47
2.3	0.5	125	3,000+
11.6	0	125	3,000+
11.6	0.5	125	3,000+

As will be evident, the additive provides long wear times compared to clear mineral oil. Also, it will be evident that while the wear time increases with the percentage increase in the amount of lead, the additive is effective even in such small concentrations as 0.01% lead.

A second type of 4-Ball Test, using a commercial non-additive lubricating oil was designed to measure the protection against scuffing or seizure afforded by the oil under extreme pressure (E.P.) conditions of boundary lubrication. In this test, a series of separate runs, each one for one hour, was carried out at different loads progressively increasing up to a maximum of 50 kg. The oil temperature was 110° C. or 75° C.; the rotational speed was 1800 r.p.m. Upon reaching a 'critical load" the one-hour scar diameter increased abruptly from about 0.5 mm. to 1.5–2 mm., as a result of scuffing and seizure. This critical load test constitutes an important evaluation of automotive engine oils, for which a critical load of 45 kg. is sometimes chosen as the minimum acceptable.

Compounds 2, 7, 11 and 15 were selected for submission to this critical load test, as shown in Table V.

TABLE V

[Critical load tests at 110° C. for 60 minutes]

	SAE 20			Mineral oil		
Base oil:						
Compound	[1]2	2	7	2	11	15
Percent lead	1.0	1.0	1.0	0.2	0.2	0.2
Percent antioxidant A	0.6	0.6	0.6	0.5	0	0
Load, kg.:						
35		—, .33				
40	.31	—, .38		.82	.85	.90
45	.33	.35, .81	.67			
50	.38	.83, .96	.71	1.13	1.06	1.01
	Estimated critical load, kg.					
	>50	50	>50	45	46	48

[1] At 75° C.

A control test in which antioxidant was present, but no lead was present, developed a scar diameter of 1.58 mm. at a 30 kg. load at 110° C. in 60 minutes. At 40 kg. load the scar diameter was 1.86 mm. The estimated critical load was 26 kg.

It will be noted that when the concentration of lead was reduced to the low level of 0.2%, the critical loads for compounds 2, 11 and 15 were still in a satisfactory range; i.e., above 44 kg. Doubling the amount of antioxidant A was of no further benefit to compound 2. At 75° C. there was comparatively little wear in the presence of compound 2, even at 50 kg. load. Compound 7 was somewhat more effective than compound 2.

In addition to an antiwear agent and an antioxidant, a detergent-dispersant additive inter alia is also recommended for a finished premium motor oil. It was found that the compounds of this invention were entirely compatible with known detergent dispersants, as for example, 2.0% Oronite 1200, a commercial ashless-type material which is a reaction product of alkenyl succinic anhydride and tetraethylene pentamine wherein the alkenyl radical has a molecular weight about 1000–1200. Further, the compounds of the invention were also compatible with rust inhibitors, commonly used in present day automotive engine oils, as for example 0.5% Bryton C–45 (a commercial material comprising an overbased calcium sulfonate, molecular weight 400–600). Further, under some conditions of use, a well-known corrosion inhibitor may be used with advantage, as for example, 0.5% Amoco 48 (a commercial material of unspecified composition, believed to be a sulfurized terpene). The latter type additive is particularly useful where the oil will come into contact with copper, as for example, in the bearings or shaft. In lubricants containing such additives as specified above, the amount of lead compound required may vary from a maximum of 1% lead, based upon the weight of the oil, to as little as about 0.01%, preferably at least about 0.1%.

The antiwear effectiveness of the compounds of the invention is in no way diminished by the presence of these other useful oil additives, but may even be increased thereby. For example, wear tests were made of a commercial SAE 20 oil containing 0.5% lead as compound 2 and 1% antioxidant A, together with the detergent-dispersant, rust inhibitor, and corrosion inhibitor cited in the preceding paragraph. In the 4-Ball Test at 15 kg. load, 50° C., there was no visible wear after 3000 minutes. In the critical load test at 110° C., the scar diameter at 50 kg. load was only 0.82 mm., indicating a critical load value of over 50 kg.

The compounds of the invention, when used as additives to lubricating oil, were subjected to other known test procedures including:

(1) RUST PREVENTION TEST

This is an adaption of an established test (ASTM D–665) of the rusting tendency of turbine oils. A rough-surfaced steel spindle is immersed in the test oil for 24 hours at 140° F. and the oil kept saturated by stirring in water, or (in a modified test) with hydrochloric acid.

(2) PANEL COKER TEST

This is a thermal stability bench test developed by Ethyl Corporation, of the type widely used in other laboratories. An aluminum alloy panel 1.5 x 3.5 inches in size is heated in a closed box for 10 hours at 550° F. Once every minute, hot test oil is sprayed onto the panel in an established pattern for a period of 5 seconds. The remaining 55 seconds afford an opportunity for the oil film to form an adherent deposit of coke. At the end of the test, the appearance of the panel is observed and the total weight increase is measured.

(3) POLYVERIFORM TEST

This is a well-known bench test that measures the tendency of the oil to oxidize and the consequent corrosion of copper-lead bearings.

(4) OLDSMOBILE CAM AND TAPPET WEAR TEST

In this test a 1960 Oldsmobile engine is fitted with calibrated valve lifter springs having 50% greater force than normal and is operated under standard conditions and the amount of scuffing to the cams and valves measured.

(5) L–38 OIL OXIDATION TEST

This is similar to the polyveriform bench test above mentioned and provides a severe test of oil's resistance at high temperature and its tendency to cause copper-lead bearing corrosion.

The foregoing tests are standard and detailed descriptions thereof need not be reproduced here. The presence of compound 2, for example together with any of the other additives called for enables the lubricating oil satisfactorily to pass these several tests.

Table VI below reports the results obtained from the above-described tests for an oil containing 0.5 weight percent of lead as compound 2 and for a high-quality

commercial oil. The oil which contained compound 2 was a clear SAE 20 oil which also contained one percent antioxidant A, 2 percent Oronite 1200 detergent-dispersant, 0.5 percent Bryton C–45 rust inhibitor, and 0.5 percent Amoco 48 corrosion inhibitor. All percentages are by weight.

TABLE VI

Test procedure and observations made	Oil containing compound 2	High-quality commercial oil
(1) Panel coker:		
Weight increase, mg	7	50–200
Deposit color	(1)	(2)
(2) Polyveriform:		
Bearing weight loss, mg	8	15
Acid number	2.1	3
Percent viscosity increase, 100° F	25	80
(3) Oldsmobile cam-and tappet, average wear, inch × 10^3:		
Cams	0.18	0.2–0.3
Lifters	0.28	0.3–0.6
(4) L–38 engine:		
Bearing weight loss, mg	13.5	19
Appearance of bearing	(3)	(4)
Piston varnish rating	10	9
Acid number increase	1.6	1.8
Percent viscosity increase:		
100° F	−3.2	7
210° F	0	3

[1] None.
[2] Tan-black.
[3] Clean.
[4] Dull or Bright.

Even concentrations smaller than reported above in Table VI, such as 0.1% lead as compound 2, have proven satisfactory in the Panel Coker Test. Using an SAE 10 oil containing 0.5% antioxidant, clear deposits of only 7 mg. were obtained. Similarly, 0.1% lead as compound 11 produced tan deposits weighing 33 mg. in the Panel Coker Test using mineral oil and 0.1% antioxidant.

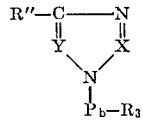
Lubricating oil containing compound 2 was also added to isooctane for the lubrication of a two-cycle outboard engine and proved to be a powerful antiwear agent. As little as 0.047% lead in the oil or 18 parts per million in the fuel-oil blend completely prevented wear. One-half this amount produced substantial reduction thereof.

What is claimed is:

1. A composition consisting essentially of a hydrocarbon lubricating oil or grease in lubricating amounts and an additive therefor in wearing reducing consisting essentially of the compound of the class consisting of

(a) trialkylplumbyl cyanamide and trialkylplumbyl cyanoguanidine in which the alkyl group has 1 to 12 carbon atoms;

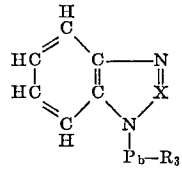
(b)



wherein

X=N, CH or CR'
Y=CH, CØ, CR, or N when X is CH or CR'
R=alkyl or 1 to 12 carbon atoms
R'=phenyl and alkyl of 1 to 20 carbon atoms
R''=H, NH_2, NHR''', alkyl having 1 to 4 carbon atoms, or phenyl
R'''=phenyl and alkyl of 1 to 20 carbon atoms
Ø=phenyl

(c)



wherein X and R have the meaning defined above under (b), but the total number of carbon atoms included in the group R and R' is at least 8.

2. The composition of claim 1, in combination with an oil soluble antioxidant.

3. The composition of claim 2, in which the antioxidant is bis(alkyl, hydroxyphenyl)methylene, present in the amount of about 0.1 to 1.0 percent by weight.

4. The composition of claim 1, in which the organolead nitrogen compound is present in the amount of at least about 0.01 percent by weight, calculated as lead.

5. The composition of claim 1 in which the organolead nitrogen compound is N-(trimethylplumbyl)cyanamide.

6. The composition of claim 1 in which the organolead nitrogen compound is N-(tributylplumbyl)imidazole.

7. The composition of claim 1 in which the organolead nitrogen compound is N-(tributylplumbyl)benzimidazole.

8. The compound of claim 1 in which the organolead nitrogen compound is 3 - amino - N - (tributylplumbyl)-1,2,4-triazole.

9. The composition of claim 1 in which the organolead nitrogen compound is 3 - anilino 5 - isopropyl - N - (tributylplumbyl)-1,2,4-triazole.

10. The composition of claim 1 in which the organolead nitrogen compound is 3-amino-5-phenyl-N-(tributylplumbyl)-1,2,4-triazole.

11. The composition of claim 1 in which the organolead nitrogen compound is N-(tributylplumbyl)benzotriazole.

12. The composition of claim 1 in which the organolead nitrogen compound is N-(triethylplumbyl)4,5-diphenylimidazole.

13. The composition of claim 1 in which the organolead nitrogen compound is N-(tributylplumbyl)-2-undecylbenzimidazole.

14. The composition of claim 1 in which the organolead nitrogen compound is N-(triethylplumbyl)-2-methyl imidazole.

15. The composition of claim 1 in which the organolead nitrogen compound is N-(triethylplumbyl)-4-methyl-5-(1-ethyl-pentyl)imidazole.

16. The composition of claim 1 in which the organolead nitrogen compound is N - (triethylplumbyl) - 2 - undecyl imidazole.

17. The composition of claim 16 in which the undecyl group of the organolead nitrogen compound is branched chain.

18. The composition of claim 1 in which the organolead nitrogen compound is N-(triisobutylplumbyl)imidazole.

19. The composition of claim 1 in which the organolead nitrogen compound is N-(triethylplumbyl)imidazole.

20. The composition of claim 1 in which the organolead nitrogen compound is an N-(trialkylplumbyl)cyanoguanidine, said alkyl group having 1 to about 12 carbon atoms.

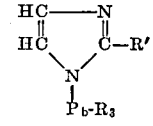
21. The composition of claim 20 in which the alkyl group is ethyl.

22. The composition of claim 20 in which the alkyl group is butyl.

23. The composition of claim 20 in which the alkyl group is heptyl.

24. The composition of claim 1 in which the organolead nitrogen compound is N-(trialkylplumbyl)imidazole in which the alkyl group has 1 to 12 carbon atoms.

25. The composition of claim 1 in which the organolead nitrogen compound is N-(trialkylplumbyl)imidazole



in which R is alkyl having 1 to 12 carbon atoms and R' is alkyl having 1 to 20 carbon atoms.

26. The composition of claim 1 in which the organolead nitrogen compound is N-(triheptylplumbyl)imidazole.

27. The composition of claim 2, plus a corrosion inhibitor.

28. The composition of claim 2 which includes a detergent-dispersant.

29. The composition of claim 1, in which the organolead nitrogen compound is present in the amount of at least about 0.1 percent by weight, calculated as lead.

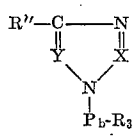
30. The composition of claim 1 in which the organolead nitrogen compound is N-(triethylplumbyl)-2-ethyl-4-methyl imidazole.

31. The composition of claim 1 in which Y is CH, CØ, or N when X is CH or CR'.

32. A composition consisting essentially of a lubricating oil or grease in lubricating amounts and an additive therefor in wearing reducing amounts consisting essentially of the compound of the class consisting of

(a) trialkylplumbyl cyanamide and trialkylplumbylcyanoguanidine in which the alkkyl group has 1 to 12 carbon atoms;

(b)



wherein

X=N, CH or CR'

Y=CH, CØ, CR, or N when X is CH or CR'

R=alkyl or 1 to 12 carbon atoms

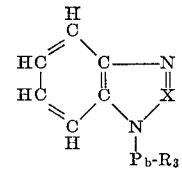
R'=phenyl and alkyl of 1 to 20 carbon atoms

R''=H, NH_2, NHR''', alkyl having 1 to 4 carbon atoms, or phenyl

R'''=phenyl and alkyl of 1 to 20 carbon atoms

Ø=phenyl

(c)



wherein X and R have the meaning defined above under (b), but the total number of carbon atoms included in the group R and R' is at least 8.

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U.S. Cl. X.R.

252—33.6; 260—437

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(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,527,704 Dated September 8, 1970

Inventor(s) Warren L. Perilstein and Harold A. Beatty

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 5, line 69, change "stiripped" to -- stripped --;
Column 7, line 67, change "AISI 521000" to -- AISI 52100 --;
Column 8, line 9, change "designated by Bayol" to -- designated Bayol --;
Column 8, Table III, (column 7) change "antioxidant" to -- antioxidant A --;
Column 8, Table III, Item 12, column 6, change "150 K" to -- 150 --;
Column 11, Claim 1, line 3, change "wearing reducing" to -- wearing reducing amounts --;
Column 12, Claim 8, line 1, change "compound" to -- -- composition --;
Column 13, Claim 32, line 6, change "alkkyl" to -- alkyl --.

Signed and sealed this 4th day of May 1971.

(SEAL)
Attest:

EDWARD M.FLETCHER, JR.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents