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FUEL AND LUBRICATING OIL COMPOSITIONS

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17 Claims. (Cl. 252—54)

The present invention relates to improved fuel and lubricating oil compositions for internal combustion engines e.g. two-stroke and four-stroke engines.

It is well-known that the accumulation of deposits in the combustion chambers of internal combustion engines brings about a considerable increase in the octane number requirement of the engine. In particular it has been found that vehicles after initial running, normally require petrol with an increase octane number over that required to begin with. Deposits formed in the engine are also accompanied by loss of power output, which may be as much as 10% or more. Further, fouling of the plugs occurs which can lead to stoppage on pre-ignition.

Certain additives, such as lead compounds, which are employed to raise the octane number of the fuel employed in the engine also play their part in producing deposits in the combustion chamber. This may occur even if detergents are used. Furthermore, the operation of internal combustion engines is also interfered with by carburettor icing. This occurs in particular when the engine is idling in a humid atmosphere having a temperature of less than 16° C., and can result in stalling of the engine due to fuel starvation.

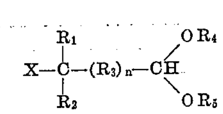
Two-stroke engines are at present generally lubricated with detergent or non-detergent lubricating oils, the oils being blended with the fuel. These compositions generally produce deposits in two-stroke engines which cause spark plug fouling, marked wearing of the valves and of the crank shaft, progressive obstruction of the exhaust port, and loss of power.

It has now been discovered that by the addition of certain additives, hereinafter described, to fuel or lubricating oils, many of the above disadvantages may be overcome.

The additives used in the compositions according to the present invention are halogenated aliphatic compounds containing one or more alcohol groups, ether groups, aldehyde groups, or ketone groups, or mixtures of two more of such groups. The compounds may have straight or branched chain structures and may be saturated or unsaturated. Chlorinated compounds are especially preferred.

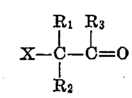
Examples of suitable compounds are those of the following general formulae:

(1) CHLORINATED ALCOHOLS AND ETHERS



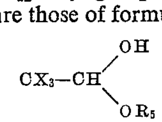
where X is halogen, R_1 and R_2 are the same halogen as X, hydrogen or an alkyl group, R_3 is an alkylene group, R_4 is hydrogen or an alkyl group, R_5 is hydrogen or an aliphatic group, and n is 0 or1. The radicals R_1, R_2, R_3, R_4 and R_5 may contain such constituents as sulfhydril, alkoxy and nitrile groups.

(2) CHLORINATED ALDEHYDES AND KETONES



where X is halogen, R_1 and R_2 are the same halogen as X, or hydrogen or an aliphatic group, and R_3 is hydrogen, a methyl group, or a chloromethyl group.

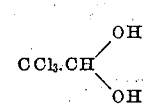
In Formula 1, R_5 is preferably a C_1 to C_{20} alkyl group, particularly a C_4 to C_{12} alkyl group. The preferred compounds in this class are those of formula



where R_5 is C_1 to C_{20} alkyl.

Examples of these compounds are chloral ethyl alcoholate, and chloral iso-amyl alcoholate. Compounds in which R_5 is a C_8 or higher alkyl radical may also be used, and have the advantage of being liquid, but insoluble in water. This makes the compounds easier to mix with the fuel and lessens the risk of having the additive content of the fuel lessened in the event of storage in the presence of water.

Another preferred compound falling within Formula 1 is chloral hydrate:



Examples of compounds of Formula 2 are chloral, $CCl_3.CHO$, compounds of formula $R.C.Cl_2.CHO$, where R is an aliphatic hydrocarbon radical, and chlorinated acetones, e.g. $Cl.CH_2.CO.CH_3$ and $Cl.CH_2.CO.CH_2.Cl$.

The fuel oil may be a gasoline, e. g. having a final boiling point of up to 300° C. In fuel compositions the additive may conveniently be present in proportions of from 0.001% to 1%, particularly 0.01% to 0.2% by weight based on the total composition.

The additives hereinbefore described may also be incorporated in lubricating oils to produce compositions according to the present invention. Such oils may be paraffinic or naphthenic in nature, and are preferably solvent-treated oils. The oils may have a viscosity of 76 to 329 cs. at 50° C. Lubricating oils intended for use in two-stroke engines may conveniently be diluted with an oil of lower viscosity, e.g. kerosene, spindle oil, or gas oil to facilitate admixture with the fuel. Thus the viscosity of the lighter oil may be between 1 and 22 cs. at 50° C. Such a mixture may contain between 50 and 70% of diluent oil.

The quantity of the additive added to the lubricating oil may be a minor proportion e.g. between 0.1 and 50%, preferably between 0.2 and 10% by weight, based on the total lubricating oil (i.e. excluding any diluent present). From 2 to 10% of the lubricating oil may be blended with fuel for use in a two-stroke engine and the amount of additive in this total oil/fuel blend may be 0.02 to 0.1%, preferably 0.05 to 0.1%.

The lubricating oil composition may also be used in the top cylinder lubrication of four-stroke engines, in which case the lubricating oil may be a low boiling petroleum oil or a synthetic oil, preferably with a viscosity of 5 to 30 cs. at 50° C. In this application, the quantity of additive added to the oil may be from 0.1 to 50%, preferably 0.5 to 10% by weight in relation to the lubricating composition. These lubricants may be blended with the fuel in proportions of 0.1 to 1%.

The compositions of this invention may also contain various optional ingredients, e. g. oiliness agents, resin (gum) solvents, anti-knock agents, anti-oxidants, anti-rust agents, metal deactivators and scavengers.

The invention may be illustrated by the following examples.

Example 1

Bench tests were carried out on a Renault engine having the following characteristics:

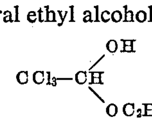
Number of cylinders	4.
Bore and stroke in mm.	58 x 80.
Rated output in H.P.	5.
Maximum output in H.P.	26.5 at 4,250 r.p.m.
Cylinder capacity in cc.	845.
Compression ratio	7.25.

In the course of these tests, periods of operation each of 5½ hours followed one another as follows:

Conditions of operation	Part I	Period of 5½ hours	
		Part II	Part III
Time in hours	1½	2	2
Speed in r.p.m.	600	2,400	2,400
Output in h.p.	0	7.2	7.2
Temperature in °C.:			
Water outlet	46±3	70±3	70±3
Crank case oil	46±3	80±3	85±3

After a first draining carried out after 150 hours' running, draining was then carried out every 44 hours (vis.: every 8 periods).

The tests were carried out with a fuel with and without the addition of chloral ethyl alcoholate.



The fuel employed was a high-grade fuel having the following characteristics:

Density at 15° C.	0.720.
Final distillation point	180° C.
Lead tetraethyl	0.45 cc./litre.
Octane number (research method)	90.
Reid vapour pressure at 38° C.	706 g./sq. cm.

The tests yielded the following results:

OCTANE NUMBER REQUIREMENT (MEASURED BY THE APPEARANCE OF TRACES OF PINKING)

	Fuel alone	Fuel plus 0.4 g. chloral ethyl alcoholate per litre
Initially	71	71
After 210 hours' running	81	77
Increase in demand	10	6

Example 2

Road tests were carried out with two Renault cars ("Dauphine") one using the fuel alone, the other plus the additive according to the invention. These two cars were used together under normal driving conditions on the road, with the leading car regularly changed. The tests were commenced with cars whose engines were perfectly clean. After a certain number of kilometres, the octane number demand ceases to increase and attains a maximum which corresponds to a kind of engine balance. The octane demand is measured by the traditional methods at the start and in the state of equilibrium.

These tests were conducted by using:

(1) A high-grade fuel containing more lead than the commercial high-grade fuels, so as to show the efficacy of the additive from the point of view of the elimination of deposits, and having the following characteristics:

Density at 115° C.	0.722.
Final distillation point	181° C.
Lead tetraethyl	0.8 cc./litre.
Octane number (research method)	94.
Reid vapour pressure at 38° C.	500 g./sq. cm.

(2) The same high-grade fuel with the addition of 0.7 g. per litre chloral ethyl alcoholate.

The tests yielded the following results:

	Octane number demand	
	High grade fuel alone	High grade fuel plus 0.7 g. chloral ethyl alcoholate per litre
Initially	70	70
At equilibrium	85	76
Increase in demand	15	6

Example 3

Tests were carried out on the road under normal driving conditions with cars that had already run without their engines having been decarbonised.

These cars were supplied with the same high grade fuel as in Example 2 (i.e. a premium fuel whose TEL content was raised to 0.8 cc. per litre), plus 0.7 g. chloral ethyl alcoholate.

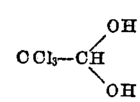
After 4000 km. the octane demand of the vehicle was measured to compare it with the initial demand.

Type of vehicle	Initial	Octane demand after 4,000 km.	Reduction
Versailles	70	64	6
Simca Aronde	76	74	2
Renault 4 H.P.	83.5	77	6.5
Renault Dauphine	85	78	7
Renault Fregate	89	85	4
Peugeot 403	78	68	10
Citröen 2 H.P.	79	76.5	2.5

This table shows the efficacy of the fuel improved according to the invention from the point of view of the lowering of the octane demand even when used for supplying a vehicle that has already run, without it being necessary to decarbonise the engine.

Example 4

Similar tests to those of Example 1, were carried out by using a fuel with and without the addition of chloral hydrate:



The fuel used was an ordinary motor spirit having the following characteristics:

Density at 15° C.	0.726.
Final point of distillation	198° C.
Lead tetraethyl	0.5 cc./litre.
Sulphur	0.7%.
Octane number (research method)	80.1.
Reid vapour pressure at 37.8° C.	580 g. sq. cm.

Use was made of chloral hydrate in the form of an alcoholic solution: 375 g. chloral hydrate are dissolved in a litre of alcohol, e.g. ethyl alcohol. The quantity added of this solution is such that the amount of chloral hydrate added to the fuel corresponds to 0.75 g. of the pure product per litre of fuel.

After running the engine for several hours, it was possible to note that the deposits in the combustion chambers were:

Without additive, hard and pale
With additive, pale, flaky and friable

As the friability of the deposits affects their adherence, it follows that in the state of equilibrium these deposits are less when the engine is supplied with a fuel containing the additive according to the invention. There follows from this an appreciable reduction in the octane demand, as shown by the results summed up in the following table:

	Octane requirement (measured by the occurrence of slight pinking)	
	Fuel only	Fuel plus chloral hydrate
Initially	62/63	65
After 210 hours running	82/85	75
Increase in demand	20/23	10
Gain in demand with fuel plus chloral hydrate		10

The improvement in the cleanliness of the engine is demonstrated by the following table in which the cleanliness of the different parts of the engine after 210 hours' running was expressed by a demerit rating ranging from 0 to 100.

This demerit rating was obtained by multiplying: a rating from 0 to 10 characterising the thickness of the deposit (0=no deposit—10 very thick deposit), by a rating from 0 to 10 characterising the surface of the deposit (0 no deposit—10 part entirely covered by deposit).

	Demerit rating	
	Fuel only	Fuel plus chloral hydrate
Combustion chamber	55.8	33.6
Valves	19	15
Rings	22.1	22
Gumming of rings	0	0
Piston skirts	3.1	2.8
Backing off of piston	18	8
Inside of piston	15	9.9
Liners	6.4	4
Sludge and sundry deposits on other parts of engine	15	4.5

Example 5

Road tests were carried out on two Renault (Dauphine) cars, one using fuel alone, and the other fuel plus the additive of the invention.

These vehicles were used together under conditions corresponding to "door to door" delivery, i.e. short distance at low speed followed by stops, engine idling or stopped and so on, a method of use which obviously furthers deposit formation. These tests were conducted at quite a low temperature. After a certain number of kilometres covered under these conditions, the octane demand was measured by the conventional methods.

These tests were carried out using as fuel:

(1) A premium fuel containing more lead than commercial premium fuels, so as to show the efficacy of the additive from the point of view of eliminating deposits, which premium fuel had the following characteristics:

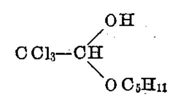
Density at 15° C. ---------------- 0.722.
Final distillation point ------------ 181° C.
Lead tetraethyl ------------------ 0.8 cc./litre.
Sulphur ------------------------ 0.05%.
Octane number (research method) ---- 91.
Reid vapour tension at 37.8° C.------- 500 g./cc.

(2) The same premium fuel with the addition of 0.75 g. chloral hydrate:

Kilometres on "door to door" service	Increase in the octane number demand			
	Fuel only, advance timing		Fuel plus chloral hydrate, advance timing	
	5°	10°	5°	10°
1,000	0	0	0	0
1,800	4	5	0	0
2,200	7	8	0	1
3,000	6	7	2	2
3,600	12	12	6	5

Example 6

In this example chloral isoamylate (or isoamyl alcoholate) was used as the additive:



The tests were carried out on the engine of a "Vespa" (124.8 cm.³ cylinder 4.5 H.P.). The engine was turned to full charge (3,000 r.p.m.) for 30 hours assuring the supply with a large amount of a commercial fuel (having an octane index of 90 research method), mixed with 3% of a lubricating oil with and without the additive. The lubricating oil has:

A density of 0.894
A viscosity index of 80
A viscosity at 37.8° C. of 305 and at 99° C. of 19.7 cs.

These tests prove:

(1) The cleanliness of the engine (piston ring wear, formation of varnish on the pistons) measured by a demerit rating ranging from 0 to 100, corresponding to an engine deposit-free, and 100 to an engine entirely encrusted with dirt.

(2) The wear of the piston rings measured by the loss of weight in mg.

(3) The importance of the deposits in grams.

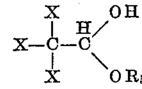
(4) The reduction of the section of the exhaust port in percent.

These tests have given the following results:

	Oil without additive	Oil plus 3% by weight of chloral isoamylate
Cleanliness (expressed as a demerit):		
Varnished piston (exterior)	5.4	7.5
Varnished piston (interior)	20.5	8.5
Wear of piston rings in mg	7.8	8.5
Deposits in g.:		
Exhaust chamber	11	9
Deposits in breech	1.52	0.58
Exhaust port	2.3	0.99
Percent blocking if exhaust port	8	Traces

What is claimed is:

1. A gasoline fuel to which has been added from 0.001 to 1.0% by weight of a compound having the formula



wherein X is a halogen atom and R_5 is selected from the group consisting of hydrogen and an alkyl group of from 1 to 20 carbon atoms.

2. A fuel as defined in claim 1 wherein said fuel contains additionally from 0.1 to 10% by weight of a lubricating oil having a visocity of from about 1 to about 330 centistokes at 50° C.

3. A fuel as defined by claim 1 wherein said R_5 contains from 4 to 12 carbon atoms.

4. A fuel as defined by claim 1 wherein said compound is present from 0.01 to 0.2% by weight of the total fuel composition.

5. A fuel as defined in claim 1 wherein X is a chlorine atom.

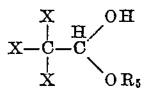
6. A gasoline fuel to which has been added between 0.001 and 1.0% by weight of chloral iso-amyl alcoholate.

7. A gasoline fuel to which has been added between 0.001 and 1.0% by weight of chloral ethyl alcoholate.

8. A gasoline fuel to which has been added between 0.001 and 1.0% by weight of chloral hydrate.

9. A gasoline fuel to which has been added between 0.01 and 0.2% by weight of chloral iso-amylate and between 2 and 10% by weight of a lubricating oil having a viscosity of about 305 cps. at 37.8° C.

10. A lubricating oil for use in internal combustion engines having a viscosity of between 76 and 329 cps. at 50° C. to to which has been added between 0.2 and 10% by weight of a compound having the formula:



wherein X is a halogen atom and R_5 is selected from the group consisting of hydrogen and an alykyl group of from 1 to 20 carbon atoms.

11. A lubricating oil composition as defined by claim 10 wherein said R_5 contains from 4 to 12 carbon atoms.

12. A lubricating oil as defined by claim 10 wherein said oil has been diluted with from 50 to 70% by weight of a lubricating oil of between 1 and 22 cps. viscosity at 50° C.

13. A lubricating oil as defined by claim 10 wherein said oil is a solvent treated paraffinic oil.

14. A lubricating oil as defined by claim 10 wherein said oil is a solvent treated naphthenic oil.

15. A lubricating oil having a viscosity of between 76 and 329 cps. at 50° C. to which has been added between 0.2 and 10% by weight of choral iso-amyl alcoholate.

16. A lubricating oil having a viscosity of between 76 and 329 cps. at 50° C. to which has been added between 0.2 and 10% by weight of chloral ethyl alcoholate.

17. A lubricating oil having a viscosity of between 76 and 329 cps. at 50° C. to which has been added between 0.2 and 10% by weight of chloral hydrate.

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