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2,863,747

MARINE WHITE GASOLINE COMPOSITIONS CONTAINING OIL-SOLUBLE ALKYLAMMONIUM DI-ALKYL ORTHOPHOSPHATES

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This invention relates to marine white gasoline compositions containing oil-soluble alkylammonium dialkyl orthophosphates.

Good quality marine white gasolines are distinguished from ordinary gasolines principally by their unleaded, substantially olefinic hydrocarbon-free character. The former must be essentially free from olefinic hydrocarbons because of the high degree of stability required of marine gasolines. In this connection it may be noted that power boat owners and operators customarily allow unused gasoline to remain in the fuel tanks of the boats during off-season periods and other periods of non-use, which periods may last for several months. During such protracted periods, unstable, olefinic hydrocarbon-containing gasolines normally will tend to darken in color and to form gums, even though oxidation and gum inhibitors may have been originally incorporated therein.

Although the time alone involved in protracted storage will place severe demands upon the stability of marine grade gasolines, these demands are made even more severe by the wide usage of copper fuel tanks in power boats, since copper tends to catalyze gum formation in gasoline.

On account of stability requirements, therefore, good quality marine gasolines will normally comprise essentially saturated gasoline hydrocarbon components and will normally be free from unstable cracked stocks, or other olefin or diolefin containing stocks.

The use of lead anti-knock agents, such as tetraethyl lead, in marine gasolines is undesirable because of the characteristic conditions under which marine engines are customarily operated. More particularly, marine engines are normally operated over the major portion of their useful lives at high, constant speeds and under heavy loads. Under such conditions leaded gasolines tend to form engine deposits that cause excessive spark plug fouling, power loss, preignition and the like.

The presence of lead in marine gasoline is additionally undesirable because of stains imparted to boat hulls and decks by the dyes required by law to be included in leaded gasolines.

Although freedom from lead is important in marine gasolines for the reasons indicated above, it has been found that the use of unleaded gasolines in internal combustion engines at the high speeds and under the heavy loads that are the rule in marine engine operation involves a severe exhaust valve seat wear problem. The severity of the exhaust valve seat wear problem in marine engine operation may be due in part to the fact that operation of an engine at high speeds and under heavy loads involves high fuel consumption with a resultant high evolution of heat and high exhaust valve seat temperatures. These high temperatures might be expected to reduce the strength of the metal exhaust valve seats at the time when the number of engine R. P. M., and therefore the number of impacts of the exhaust valves with the exhaust valve seats, are high. Thus, an oppor-

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tunity for severe exhaust valve seat wear might be expected under normal conditions of marine engine operation.

It is to be noted that the problem of severe exhaust valve seat wear in marine engines is unique to unleaded gasolines, there being no severe wear problem when leaded gasolines are used. Evidently, lead deposits resulting from the combustion of leaded gasolines tend to condition the exhaust valve seats in such a way as to increase their wear resistance. In this connection, the exhaust valve seats of marine engines operated on leaded gasolines have been observed to possess a somewhat glazed appearance that is distinctly different from the appearance of the exhaust valve seats of marine engines following operation with unleaded gasolines.

Thus, despite the fact that severe exhaust valve seat wear in marine engines can be substantially avoided by the use of leaded gasolines, such gasolines are for other reasons sufficiently undesirable as to prevent the use of lead anti-knock agents in good quality marine gasolines.

We have found that severe exhaust valve seat wear in marine engine operation can be reduced by incorporation in an unleaded, olefinic hydrocarbon-free marine gasoline that normally tends to permit severe exhaust valve seat wear of a small amount of a substantially neutral addition salt such as n-dodecyl amine or cocoamine and a dialkyl acid orthophosphate whose alkyl groups are selected from the group consisting of 3-methylbutyl, 2-ethylhexyl, mixed branched-chain octyl, and mixed branched-chain amyl radicals. The present invention includes gasoline compositions of this kind as well as the method of operating a marine engine using such gasoline compositions.

The exact manner in which the alkylammonium dialkyl orthophosphates disclosed herein function to reduce wear of exhaust valve seats in marine engines has not been fully ascertained. Although the invention is not dependent upon or limited to any particular theory of operation it may be that the combustion products of the herein disclosed alkylammonium dialkyl orthophosphates tend to act, either physically or chemically, or both, upon the metal exhaust valve seats to render the latter more wear-resistant.

The substantially neutral alkylammonium dialkyl orthophosphates having use in the gasoline compositions of this invention can be prepared in any convenient manner. For example, they can be prepared by reacting a suitable dialkyl acid orthophosphate with substantially equimolar proportions, or sufficient to produce a pH of about 5.5-7.5, of one or more suitable primary n-alkyl amines according to the method disclosed in U. S. Patent No. 2,387,537.

A preferred primary n-alkyl amine that forms addition salts useful in the compositions of this invention is n-dodecyl amine. It is not necessary that the amine be in pure form, and other amines can be admixed therewith. In fact, excellent results have been obtained with addition salts prepared from a mixture of n-dodecyl amine and other primary n-alkyl amines. An example of a commercial mixture of amines that forms unusually effective addition salts with the dialkyl acid orthophosphates disclosed herein is cocoamine. Cocoamine is a mixture of primary n-alkyl amines derived from coconut oil fatty acids and has a normal mol combining weight of about 210 and a melting point of about 21° C., and is composed principally of n-dodecyl amine together with lesser amounts of other primary straight chain amines containing an even number of carbon atoms from 8 to 18.

An example of a dialkyl acid orthophosphate that forms especially effective addition salts with the primary

n-alkyl amines indicated above is the 3-methylbutyl, 2-ethylhexyl acid orthophosphate. Examples of other dialkyl acid orthophosphates that can be used to prepare addition salts with the amines indicated above are dialkyl acid orthophosphates whose alkyl groups are derived from C₅ and C₈ Oxo alcohols, which as is known are predominantly branched chain saturated aliphatic monohydric alcohols prepared by the "Oxo-Synthesis" process, a process that involves the hydroformylation of olefinic hydrocarbons with hydrogen and carbon monoxide, followed by hydrogenation of the carbonylic compounds thus obtained. By way of example, the C₈ Oxo alcohols normally consist mostly of isomeric dimethyl hexanols, and the C₅ Oxo alcohols normally consist mostly of isomeric methyl butanols. Specific examples of other dialkyl acid orthophosphates that are capable of forming suitable salts for the purposes of this invention are the bis-(3-methylbutyl) acid orthophosphate and the bis-(2-ethylhexyl) acid orthophosphate.

A specific example of an especially effective, and therefore preferred, alkylammonium dialkyl orthophosphate composition for the purposes of this invention is the substantially neutral addition salt of cocoamine and 3-methylbutyl, 2-ethylhexyl acid orthophosphate. A specific example of an effective, single addition salt, the use of which is included by the invention, is the substantially neutral addition salt of n-dodecyl amine and 3-methylbutyl, 2-ethylhexyl acid orthophosphate.

The foregoing salts as well as other of the disclosed class can be prepared as described in the aforementioned U. S. Patent No. 2,387,537, with the substitution of equivalent amounts of the appropriate n-alkyl amines and dialkyl acid orthophosphates.

The n-alkylammonium dialkyl orthophosphates that are useful for the purposes of this invention can be incorporated in the marine gasoline disclosed herein in any suitable manner. For example they can be added as such to the marine gasoline, or they may be added in the form of concentrated mineral oil solutions, an example of which is disclosed in U. S. Patent No. 2,387,537. Although some stirring may be desirable during incorporation of the salts in the gasolines, in order to produce a homogeneous mixture more rapidly, stirring is not essential. In the case of blended marine gasoline the inhibitor selected for use can be added to one component of the ultimate blend prior to the mixing of this component with the other component or components of the blend. Also, the inhibitors can be prepared in situ, if desired.

The n-alkylammonium dialkyl orthophosphates disclosed herein are useful in marine gasolines of the class disclosed herein when used in concentrations sufficient to reduce the exhaust valve seat wear of internal combustion engines. Some benefits to the gasoline can be observed after incorporation in the gasoline of as little as 3 pounds of the salt per thousand barrels of gasoline, i. e., about 0.001 percent by weight. Excellent results with respect to exhaust valve seat wear reduction have been obtained by the use in marine gasoline of about 10 to about 20 pounds of the amine salt per thousand barrels of gasoline. Although larger proportions of the herein disclosed salts, for example, up to 30 pounds or more per thousand barrels of gasoline, can be used, such proportions are normally unnecessary for the purposes of this invention.

Gasolines to which there can be added the n-alkylammonium dialkyl orthophosphates disclosed herein and whose use is included by this invention are the stocks that are especially prepared for use in marine engines and that tend to induce exhaust valve seat wear in marine engines. As indicated previously, such gasolines are hydrocarbon mixtures boiling within the gasoline range that are characterized chiefly by their freedom from lead anti-knock agents, e. g., tetraethyl lead, and by their freedom from olefinic hydrocarbons. By "olefinic hydrocarbon" is

meant any hydrocarbon compound containing an olefinic (ethylenic) linkage between two adjacent carbon atoms. Gasolines that are free or essentially free from olefinic hydrocarbons are characterized by a low bromine number, e. g., not greater than about 5. The gasoline boiling range is defined by Gruse and Stevens in Chemical Technology of Petroleum, McGraw-Hill, 1942, page 450, as 100° to 400° F. Examples of essentially olefinic hydrocarbon-free gasolines are straight run gasoline derived from crude petroleum and alkylate gasoline, which, as is known, is composed of isoparaffins derived by alkylation of paraffin hydrocarbons with olefins. Thermally cracked gasolines and polymerized gasolines which contain relatively high proportions of olefinic hydrocarbons, and catalytically cracked gasolines which, although normally possessing a lower olefinic hydrocarbon content than the former, exhibit considerable tendency toward color darkening and gum formation during storage, are ordinarily unsuitable for use in good quality marine white gasolines, unless they have first been treated to saturate the olefinic linkages, as by catalytic hydrogenation, or severely treated, as by acid treating, to remove color-forming and gum-forming unsaturated bodies from the gasoline.

Other characteristics that are normally exhibited by high quality marine grade gasolines are a low Reid vapor pressure, for example, below about 7.5, preferably not more than about 7.0, in order to avoid the vapor locks that are promoted by warm inboard engine compartments, and a relatively low end distillation point, for example, not greater than about 375° F., preferably not greater than about 340° F., in order to minimize crankcase dilution due to the low crankcase and jacket coolant temperatures prevalent in marine engines, and a low sulfur constant, i. e., not more than about 0.075%.

The present invention may be more fully understood by reference to the following specific example.

Example 1

A marine white gasoline composition according to this invention and having good exhaust valve seat wear-reducing properties was prepared by admixture with an unleaded, essentially olefinic hydrocarbon-free blended stock consisting of about 80 percent straight run and about 20 percent alkylate gasoline hydrocarbons, of the substantially neutral addition salt of cocoamine and 3-methylbutyl, 2-ethylhexyl acid orthophosphate, the salt being in the form of an 84 percent solution in a mineral oil solvent. The addition salt concentrate was added to the gasoline stock in the proportion of 20 pounds per thousand barrels of gasoline. The gasoline stock of this example had the following inspections:

Gravity, ° API	68.3
Reid vapor pressure, lbs./in. ²	6.2
ASTM distillation:	
I. B. P., ° F	116
E. P., ° F	335
Percent evap., ° F.—	
10	146
50	183
90	242
Oxygen stability, hrs	>1440
TEL, cc./gal	None
Bromine No	1.6
ASTM color, mg./100 ml	<0.1
Copper dish gum, mg./100 ml	2.6
Sulfur, percent	0.005
Octane ratings:	
Motor	79.3
Research	81.2

The gasoline composition of this example also contained, as a copper deactivator, N,N'-disalicylidene-1:2 diaminopropane, in the proportion of one pound per thousand barrels of gasoline. The copper deactivator is employed in the gasoline in order to reduce the tend-

ency of the gasoline to form gum in the presence of copper, and is considered to have no effect upon the exhaust valve seat wear-reducing properties, or other beneficial properties, of the amine salts of this example.

The foregoing example is illustrative only, and other marine gasoline compositions having exhaust valve seat wear-reducing characteristics can be obtained by substituting other addition salts disclosed herein in the foregoing example, in the same or equivalent proportions.

The ability of the alkylammonium dialkyl orthophosphates disclosed herein to function in unleaded, olefinic hydrocarbon-free marine white gasolines to reduce exhaust valve seat wear under high speed, heavy load conditions has been demonstrated by accelerated engine tests

and no lash loss was found in any of the other exhaust valves.

Several additional compositions according to this invention were prepared using a white gasoline stock essentially identical with that described in detail in Example I, and having incorporated therein from 5 to 25 pounds per thousand barrels of the substantially neutral addition salt of cocoamine and 3-methylbutyl,2-ethylhexyl acid orthophosphate in the form of an 84 percent solution in mineral oil. Each of these compositions also had added thereto N,N'-disalicylidene-1:2 diaminopropane copper deactivator in the proportion of one pound per thousand barrels. These compositions possessed the properties indicated in the following table:

	Run No.					
	1	2	3	4	5	6
Make-up, Percent:						
White Gasoline Stock	100	100	100	100	100	100
Cocoamine Salt of 3-Methylbutyl,2-Ethylhexyl Acid Orthophosphate (84 Percent Mineral Oil Solution), Lb./1,000 Bbl.		5	10	16	20	25
Inspection:						
Rust Preventive Test—4 Hrs., 10 Percent Distilled Water, 80° F., Steel Rod, Rating ^a	4	0	0	0	0	0
Rust Preventive Test ^b —4 Hrs., 10 Percent Synthetic Sea Water, 80° F., Steel Rod, Rating ^a	4	4	2	1	0	0
Copper Dish Gum, Mg./100 ML	2	3	3	4	5	1
Existent Gum, Mg./100 ML, ASTM-D-381	1	2	2	2	2	6
Accelerated Gum, Mg./100 ML, MIL-F-5572	3	4	4	4	4	5
Storage Test with 1% Distilled Water Added 19 Days—						
Copper Strip, Wt. Change Mg.	-0.7			-0.4	-0.4	-0.8
Appearance of Strip	bright			bright	bright	bright

^a Rating scale: Rust—0=0%; 1=1-5%; 2=6-25%; 3=26-50%; 4=51-100%.
^b The freshly inhibited gasoline was first washed with 10% by volume of distilled water for one minute; the water was then withdrawn and the gasoline was then tested with 10% by volume of synthetic sea water as indicated.

carried out in an L-head Chris Craft 145 horsepower ML series engine. According to the test procedure followed, exhaust valve lash is adjusted to a standard setting, and the engine is then operated under simulated break-in conditions for 7 hours using the test gasoline. During the simulated break-in period the load and speed of the engine are gradually increased until a speed of 3200 R. P. M. is reached at full throttle at 7 hours. Engine operation at 3200 R. P. M. is continued for whatever number of hours is required to reach an 0.005 inch valve lash loss in any one exhaust valve. In order to determine the valve lash loss the valve lash is measured periodically during the test. Normally, the valve lash is measured at the end of 4 hours during the break-in period and every third hour thereafter. The results obtained in the tests of the uninhibited marine white gasoline stock referred to in Example I and of the marine white gasoline composition of this invention defined in Example I are presented in the following table:

Test Gasoline	Hrs. to 0.005 In. Exhaust Valve Lash Loss (Avg. of 2 Runs)
Uninhabited Marine White Gasoline Stock	6.5
Marine White Gasoline Composition of Example I	12.2

The results in the foregoing table indicate the marked reduction in exhaust valve seat wear obtainable by the use of the marine gasoline compositions of this invention.

By way of indicating the distinct nature of the exhaust valve seat wear problem in connection with unleaded gasolines it may be noted that a white gasoline, essentially identical with the base stock described in Example I, to which there had been added 3 cc. of tetraethyl lead per gallon, was tested in a Chris Craft engine according to the procedure described above. After 19 hours a valve lash loss of 0.002 in. was observed in one exhaust valve,

From the results presented in the foregoing table it will be seen that as little as 5 pounds per thousand barrels of the alkylammonium dialkyl orthophosphate concentrate provides marked resistance to rusting of ferrous metals in the presence of distilled water. The gasoline samples containing 16 to 25 pounds of the additive concentrate per thousand barrels provide marked resistance to rusting of ferrous metals that have been contacted with either distilled water or salt water. It is noted that these advantageous results are obtained concurrently with good results respecting the existing gum content, the potential gum-forming tendencies, and copper corrosiveness.

The gasoline compositions of this invention can contain in addition to the additives disclosed herein other agents designed to improve one or more properties of the gasoline. For example, the composition may contain other rust and corrosion inhibitors, anti-knock agents other than those containing lead, preignition control additives, antioxidants, gum inhibitors, detergents, de-icing agents, and the like.

We are aware that certain alkyl amine salts of organic phosphates have been suggested for use as haze inhibitors in gasolines that tend to form haze on exposure to light; thus, certain alkyl amine salts of certain organic phosphates have been suggested for use in inhibiting light-induced haze in gasolines containing tetraethyl lead. The present invention does not include such gasoline compositions and vice versa, since unleaded gasolines that are essentially free of olefinic hydrocarbons, i. e., those that can be used in the compositions of this invention, do not tend to form haze on exposure to light. By way of demonstrating the insensitivity of such gasolines to light, a sample of unleaded gasoline containing no additives, consisting of 80 percent straight run gasoline hydrocarbons and 20 percent alkylate gasoline hydrocarbons and corresponding essentially to the base stock of Example I was tested under accelerated conditions by exposure thereof in a fused quartz container to ultraviolet light in a standard Eveready C-3B carbon arc solarium unit.

Two other samples of gasoline corresponding respectively to the straight run and alkylate components of the first sample were similarly tested. No haze was detected in any of the samples after 405 minutes, after which time the tests were discontinued. This corresponds to about 20 hours' exposure to direct June sunlight at latitude 42.

Various modifications of the embodiments disclosed above can be resorted to without departure from the spirit or scope of the invention. Accordingly, the invention is to be limited only by the scope of the claims appended hereto.

We claim:

1. A gasoline composition suitable for marine use consisting essentially of a major amount of an unleaded, substantially olefinic hydrocarbon-free gasoline having an octane rating less than isooctane and a minor amount, sufficient to reduce exhaust valve seat wear in marine engine operation, of a substantially neutral addition salt of n-dodecyl amine and a dialkyl acid orthophosphate whose alkyl groups are selected from the group consisting of 3-methylbutyl, 2-ethylhexyl, and mixed branched-chain octyl and mixed branched-chain amyl radicals.

2. A gasoline composition suitable for marine use con-

sisting essentially of a major amount of an unleaded, substantially olefinic hydrocarbon-free gasoline having an octane rating less than isooctane and 10 to 20 pounds per thousand barrels of the substantially neutral addition salt of n-dodecyl amine and 3-methylbutyl, 2-ethylhexyl acid orthophosphate.

3. A gasoline composition suitable for marine use consisting essentially of a major amount of an unleaded, substantially olefinic hydrocarbon-free gasoline having an octane rating less than isooctane and 10 to 20 pounds per thousand barrels of the substantially neutral addition salt of cocoamine and 3-methylbutyl, 2-ethylhexyl acid orthophosphate.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,863,747

December 9, 1958

Troy L. Cantrell et al.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Columns 5 and 6, under Run No. "6", fifth figure, for "1" read -- 6 --; same column, sixth figure, for "6" read -- 1 --.

Signed and sealed this 10th day of March 1959.

(SEAL)

Attest:

KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents