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**AVIATION GRADE GASOLINES CONTAINING
N-ALKYL AMINE SALTS OF DIALKYL ACID
ORTHOPHOSPHATES**

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This invention relates to aviation grade gasolines containing n-alkyl amine salts of dialkyl acid orthophosphates.

Aviation engines of the reciprocating spark ignition type, of the kind used in large commercial transport aircraft, military transport aircraft, and military combat aircraft are highly sensitive to the presence of foreign particles such as rust flakes in the fuel, since the fuel systems of such engines employ filters having extremely small orifices. At the present time fuel filters having orifices of about 20 microns are customarily used in these engines and filters having 10 micron orifices are expected to come into general use in the future. It is therefore of great importance that aviation grade gasolines burned in aviation engines of the kind indicated above have rust preventive characteristics that will protect fuel storage tanks, fuel lines and other metal surfaces contacted by the gasoline against rust and corrosion.

The problem of providing rust and corrosion inhibiting properties in aviation gasolines of the kind included by this invention, that is, aviation grade fuels having an aviation lean mixture anti-knock rating of at least 100 and an aviation rich mixture anti-knock rating of at least 130, is complex, since it involves difficult problems that are peculiar to the operation of aviation engines using such fuels. Among the more important of these problems are the sensitivity of aviation engines to intake system deposits, and, in the case of high horsepower commercial and military engines of the kind that employ the fuels of this invention, the propensity of such engines to develop intake deposits. Intake deposits are a serious problem in aircraft engines, as it is essential that the aircraft be capable of developing maximum or substantially maximum rated horsepower during takeoff under heavy load conditions. The formation of intake deposits tends to reduce the maximum horsepower of the engine by restricting the intake passages and thus limiting the quantity of air and/or gasoline that can pass therethrough. The presence of intake system deposits can be evidenced by an unusually low engine manifold pressure, and this symptom calls for engine overhaul.

It is particularly noted that any tendency of the gasoline to form intake deposits will be greatly magnified in high horsepower aviation engines simply because of the large volumes of fuel that are vaporized and passed through the intake systems of these engines. By way of example, it is noted that a typical commercial aviation engine was operated for a substantial period with a fuel consumption of about 135 gallons of gasoline per hour. In contrast a typical automobile engine will consume an estimated 4 gallons or less of gasoline per hour during sustained operation. In the example cited, the tendency to form intake deposits in the aviation engine would be approximately thirty times as great.

Because of the propensity of high horsepower aviation engines to form intake deposits and because of the sensitivity of such engines thereto, it is impractical to

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employ any rust inhibitors in aviation gasoline that tend to develop excessive intake deposits in aviation engines at effective, rust inhibiting concentrations. To do so would be a great detriment, since the use of a gasoline containing such an inhibitor would necessitate costly engine overhauling at more frequent intervals than is customary in the interest of safety.

In recognition of the sensitivity of aviation engine to intake deposits and of the propensity of such engines to form these deposits, military procurement authorities, for example, require that aviation grade gasoline must be provided with satisfactory rust and corrosion inhibiting properties with inhibitor concentrations of not more than 20 pounds per thousand barrels of gasoline, that is, approximately 0.008 percent by weight. This limitation alone has the effect of eliminating a large number of oil-soluble rust and corrosion inhibitors that function effectively only in relatively large concentrations. Many other conventional oil-soluble rust and corrosion inhibitors that are relatively effective in low concentrations have proved unsatisfactory because of their intake deposit-forming tendencies. For example, metal-containing, ash-forming inhibitors will ordinarily form objectionable intake deposits because of their low volatility. However, the problem of deposits is not limited to ash-forming inhibitors. Many ashless inhibitors also cause difficulty. For example some essentially ashless inhibitors, particularly those of low pH, are objectionable, since they tend to promote gum formation in the gasoline, which in turn leads to intake deposits. Still other inhibitors, particularly those having a relatively high pH, are objectionable since they tend to cause corrosion of aluminum which is used extensively in aircraft engines. Still other inhibitors will be objectionable, either because of their own tendency to form deposits, their relative ineffectiveness as rust inhibitors or other undesirable characteristics. Sulfonates, for example, are unsatisfactory because of their poor water separation properties. Entrained moisture in aviation gasoline tends to form ice crystals in the gasoline during the rapid temperature reductions experienced by aircraft climbing to high altitudes. Such particles will tend to clog the fuel filters previously mentioned.

We have found that outstanding rust and corrosion inhibiting properties can be imparted to aviation grade gasolines of the kind used in commercial transport aircraft and military transport and combat aircraft by incorporation therein of 3 to 20 pounds per thousand barrels of gasoline of a substantially neutral addition salt of mixed primary n-alkyl amines containing 8 to 18 carbon atoms per molecule and a dialkyl acid orthophosphate whose alkyl groups are branched and contain 5 or 8 carbon atoms each. The present invention includes aviation gasoline compositions of this kind and the method of operating an aviation engine using such fuels.

The rust inhibitors having use in the gasoline compositions of this invention are prepared by reacting a suitable dialkyl acid orthophosphate with substantially equimolar proportions of one or more primary n-alkyl amines of the class indicated. The reaction is normally exothermic, and the temperature should be maintained between 140° and 200° F., and preferably below 180° F., the reaction mixture being externally cooled if necessary. The pH of the product can be adjusted to substantially neutral, by which is meant a pH of 5.5 to 7.5, preferably about 7 (as measured with a quinhydrone-calomel electrode assembly), by the use of greater or lesser than equimolar proportions of the primary n-alkyl amine. The reaction is preferably carried out in a mineral oil solvent, e. g., a lubricating oil, in order to facilitate control of the reaction and as the resulting product is in the form of

a mineral oil concentrate that is relatively easily blended with the aviation gasoline.

Amines that form suitable addition salts with the disclosed dialkyl phosphates are mixed primary n-alkyl amines containing 8 to 18 carbon atoms per molecule. In fact, excellent results have been obtained with addition salts prepared from mixtures of primary n-alkyl amines of the class indicated. An example of a commercial mixture of amines that forms outstandingly effective addition salts with the herein disclosed dialkyl orthophosphates is cocoamine, which is a mixture of primary n-alkyl amines derived from coconut oil fatty acids. Cocoamine normally has a mol combining weight of about 210, a melting point of about 21° C., and is composed principally of n-dodecyl amine together with lesser amounts of homologous, primary straight chain amines containing an even number of carbon atoms ranging from 8 to 18.

An example of a dialkyl acid orthophosphate of the class disclosed and 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 o-phosphates where the 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" 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 commonest C₈ Oxo alcohols consist mostly of isomeric dimethylhexanols, and the commonest C₅ Oxo alcohols consist mostly of isomeric methylbutanols. Specific examples of other dialkyl acid orthophosphates within the disclosed class are the bis-(3-methylbutyl)acid orthophosphate and the bis-(2-ethylhexyl)acid orthophosphate.

A specific example of an especially effective inhibitor for the purposes of the invention is the neutral addition salt (pH 7) of cocoamine and 3-methylbutyl,2-ethylhexyl acid orthophosphate.

A preferred substantially neutral salt having use in the compositions of this invention can be prepared by a typical procedure comprising introducing into a vessel, equipped with heating and cooling coils and mechanical means for agitation, about 210 parts by weight of cocoamine (Armeen CD), purchased from Armour & Company, Chicago, Illinois, and which consisted of about 47 percent n-dodecyl amine together with substantially lesser proportions of primary n-alkyl amines homologous thereto and containing even numbers of carbon atoms from 8 to 18. To the cocoamine is slowly added about 281 parts by weight of 3-methylbutyl,2-ethylhexyl acid orthophosphate in lubricating oil solution (purchased from the Victor Chemical Company), the temperature of the reaction being maintained below about 180° F. After addition of the dialkyl acid orthophosphate is complete, approximately 14 parts by weight of additional cocoamine is added to adjust the pH of the mixture to exactly 7, and the mixture stirred for about one hour. A typical product obtained by the above procedure is an 84 weight percent solution in mineral oil of the neutral salt of cocoamine and 3-methylbutyl,2-ethylhexyl acid orthophosphate, that is amber-red in color. The product is readily soluble in lubricating oil and aviation gasoline and practically insoluble in water.

The inhibitors that are useful for the purposes of this invention can be incorporated in aviation gasolines of the kind disclosed herein in any suitable manner. For example, they can be added as such or in the form of concentrated mineral oil solutions such as disclosed above. Some stirring may be desirable to produce a homogeneous mixture more rapidly, but stirring is not essential. In the case of blended gasolines the inhibitor

selected for use can be added to one component of the ultimate blend, prior to its blending with other components. In fact, the inhibitors can be prepared in situ, if desired.

The inhibitors disclosed herein are useful in aviation grade gasolines of the class disclosed when used in concentrations of 3 to 20 pounds inhibitor per thousand barrels of gasoline. Excellent results have been obtained with about 5 to 7 pounds per thousand barrels where salt water corrosion is not a problem. Where salt water corrosion is a serious problem from 15 to 20 pounds per thousand barrels should be used in order to obtain fully effective results.

Aviation gasolines customarily comprise hydrocarbon mixtures having a distillation range defined in ASTM D 910-52 T as follows: 10 percent evaporated, max. -158° F.; 50 percent evaporated, max. -221° F.; 90 percent evaporated, min. -212° F.; 90 percent evaporated, max. -257° F. Aviation grade gasolines included by this invention are those boiling within the above indicated range and having an aviation lean mixture octane rating of at least 100 and an aviation rich mixture octane rating of at least 130. Examples of aviation gasolines in this class are the so-called 100/130 and 115/145 aviation grade gasolines. Commercial gasolines of these grades normally contain 3 to 8 ml. tetraethyl lead per gallon, 1.5 to 4 ml. per gallon of a lead scavenger, for example, ethylene dibromide, 3 to 10 pounds per thousand barrels of an antioxidant, for example, of the class consisting of 2,6-di-*t*-butyl,4-methylphenol, 2,4-dimethyl-6-*t*-butylphenol and N,N'-di-secondary-butyl-p-phenylene diamine, and a dye.

The aviation grade gasolines of the class included by the invention are those normally used in the high horsepower reciprocating spark ignition engines, e. g., those developing 1000, 2000, 3000 horsepower or more, used in large commercial and military aircraft and which have a strong tendency to develop intake deposits.

EXAMPLE I

An aviation grade gasoline composition within the scope of this invention is prepared by dissolving 7 pounds per thousand barrels of an 84 percent solution in lubricating oil of a neutral salt (pH 7.0) of cocoamine and 3-methylbutyl,2-ethylhexyl acid orthophosphate in a commercial 115/145 aviation grade gasoline containing 4.55 ml. tetraethyl lead per gallon, a proportionate quantity of ethylene dibromide, and 8.4 pounds per thousand barrels of 2,6-di-*t*-butyl,4-methylphenol, a typical sample of which gasoline has the following inspections:

Distillation, °F.:

10%	-----	145
50%	-----	208
90%	-----	252

The foregoing example is illustrative only and other compositions of improved corrosion inhibiting properties and included by the invention can be obtained by substituting other addition salts disclosed herein in the foregoing example, in the same or equivalent proportions.

The ability of the inhibitors of this invention to function in aviation grade gasoline of the kind included in the scope of this invention and that is burned in a high horsepower commercial type aviation engine, without formation of objectionable intake deposits, was demonstrated by operation of a Wright aeronautical R-3350-30W radial, air-cooled compound engine using a commercial 115/145 aviation grade gasoline of the general character disclosed in Example I and containing 20 pounds per thousand barrels of an 84 percent solution in lubricating oil of the neutral (pH 7) cocoamine addition salt of 3-methylbutyl,2-ethylhexyl acid orthophosphate. The engine was operated in 11 to 13 hour periods for about four days. At the conclusion of the test the engine was examined for deposits. The induction system, intake pipes, supercharger housing and distributor tubes showed

no signs of deposits. Several cylinders were removed and examined. The intake valve seats were found to be clean and no evidence of burning or pitting was noted.

When the test was repeated using the same gasoline except containing as a rust inhibitor 20 pounds per thousand barrels of a commercial rust inhibitor previously accepted for use in aviation grade gasolines, and believed to comprise a 50 percent solution in kerosene of a dimerized linoleic acid and containing small amounts of phosphorous, sulfur and chlorine in unidentified form, and having a pH of about 2, objectionable deposits were found in cylinder intake passages and intake valve housings. The front even-numbered cylinders showed medium deposits and the rear odd-numbered cylinders showed heavy deposits. Intake valves showed heavy deposits and in some cases the deposits near the valve seats had been rubbed by contact with the sides of the intake passages. Intake pipes were covered with a heavy rippled deposit.

The rust inhibiting characteristics of the inhibitors included in the scope of the invention have been demonstrated by subjecting them to the Armed Forces test for aircraft fuel, Military Specification MIL-L-25017 (ASG), Method 4011, Procedure B. Briefly, this test involves stirring a 300 ml. sample of depolarized isooctane containing the inhibitor being tested (here the inhibitor of Example I) with 30 ml. of synthetic sea water (ASTM D 665-52 T) at a temperature of 100° F., with a cylindrical steel test specimen immersed therein. At the end of the test, rust protection can be determined by comparison of the steel test rod with a similar rod that has been subjected to the same conditions in an uninhibited sample of the reference fuel. The results of these tests are presented below. In order to illustrate the unique effectiveness of the inhibitors of this invention there are also presented below for purposes of comparison the results obtained in similar tests using various substantially neutral amine addition salts of dialkyl orthophosphates other than those within the scope of this invention.

Table A

[Make-up: 300 ml. depolarized isooctane, 30 ml. of synthetic sea water and inhibitor expressed in pounds per thousand barrels.]

Test Runs	1	2	3	4	5
Isooctyl Amine Salt of 3-methylbutyl, 2-ethylhexyl o-Phosphoric Acid (84 percent mineral oil solution)		10			
Mixed t-C ₁₂₋₁₅ branched chain Alkyl Amine (Avg. C ₁₃) Salts of 3-methylbutyl, 2-ethylhexyl o-Phosphoric Acid (84 percent mineral oil solution)			20		
Mixed n-Octadecenyl and n-Octadecadienyl Amine Salts of 3-methylbutyl, 2-ethylhexyl o-Phosphoric Acid (84 percent mineral oil solution)				20	
Cocoamine Salts of 3-methylbutyl, 2-ethylhexyl o-Phosphoric Acid (84 percent mineral oil solution)					10
Inspection; Rust:					
After 4 hours	3	3	3	2	0
After 24 hours	4	4	4	4	0

1 Rating scale:

	Rust
0	0
1	1-5%
2	6-25%
3	26-50%
4	51-100%

The data presented in the foregoing table demonstrated the unique effectiveness of the agents of this invention.

It is to be noted that the problem of imparting rust and corrosion inhibition characteristics to aviation gasoline, aside from the problem of intake deposits, is distinct from that of imparting similar properties to lubricating oils. Gasolines contain a high percentage of low-molecular weight branched chain, aromatic and olefinic components, whereas lubricating oils contain essentially saturated aliphatic, high molecular weight paraffinic and/or naphthenic components. Also gasolines tend to dissolve water more readily than do lubricating oils.

To demonstrate the distinct nature of the two problems, a sample of a highly paraffinic turbine lubricating oil containing 20 pounds per thousand barrels of the neutral salt of cocoamine and 3-methylbutyl, 2-ethylhexyl acid orthophosphate was tested according to Procedure B (synthetic sea water) of the ASTM D 665-53 T accelerated corrosion test, modified to 100° F. and 20 hours for fuels, and wherein the test sample was previously depolarized with activated alumina and washed with 10 percent by volume distilled water (MIL-I-25017 (ASG) Method 4011, Procedure B). The same test was then carried out using a 115/145 commercial aviation grade base fuel containing 20 pounds per thousand barrels of the agent used in the preceding test. At the conclusion of the tests, the test rod contacted with the turbine oil showed 90 percent rust, whereas the test rod contacted by the aviation gasoline showed only 6 percent rust. Thus, although the maximum concentration included by the invention provides essentially no rust protection in lubricating oil at the conditions of the test, excellent rust protection was imparted to aviation gasoline under the same test conditions by the same amount of additive.

The gasoline compositions of this invention can contain in addition to the additives disclosed 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, lead scavengers, preignition control additives, antioxidants, detergents, de-icing agents, dyes, and the like.

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

We claim:

1. An aviation grade gasoline comprising a major amount of a hydrocarbon mixture boiling in the aviation gasoline range and having an aviation lean mixture anti-knock rating of at least 100 and an aviation rich mixture anti-knock rating of at least 130, and containing about 3 to 20 lbs./1000 bbls. of gasoline of a substantially neutral addition salt of (a) mixed primary, n-alkyl amines containing 8 to 18 carbon atoms per molecule, the amine present in the largest proportion containing 12 carbon atoms, and (b) a dialkyl acid orthophosphate whose alkyl groups are selected from the class consisting of branched chain octyl and amyl radicals, the amount of said salt being sufficient to impart rust inhibiting properties to the gasoline during storage, said gasoline being substantially free from any tendency to deposit solids in aviation engine intake systems.

2. An aviation grade gasoline comprising a major amount of a hydrocarbon mixture boiling in the aviation gasoline range and having an aviation lean mixture anti-knock rating of at least 100 and an aviation rich mixture anti-knock rating of at least 130, and containing about 3 to 20 lbs./1000 bbls. of the substantially neutral addition salts of cocoamine and 3-methylbutyl, 2-ethylhexyl acid orthophosphate, the amount of said salt being sufficient to impart rust inhibiting properties to the gasoline during storage, said gasoline being substantially free from any tendency to deposit solids in aviation engine intake systems.

3. An aviation grade gasoline consisting essentially of a hydrocarbon mixture boiling in the aviation gasoline range and having an aviation lean mixture anti-knock rating of at least 100 and an aviation rich mixture anti-knock rating of at least 130, and containing 3 to 10 lbs./1000 bbls. of an antioxidant selected from the group consisting of 2,6-di-t-butyl, 4-methylphenol, 2,4-dimethyl-6-t-butylphenol and N,N'-di-sec-butyl-p-phenylene diamine, 3 to 8 ml. of tetraethyl lead per gallon, 1.5 to 4 ml. per gallon of ethylene dibromide, and 3 to 20 lbs./1000 bbls. of the substantially neutral addition salts of cocoamine and 3-methylbutyl, 2-ethylhexyl acid orthophos-

phate, the amount of said salts being sufficient to impart rust inhibiting properties to the gasoline during storage, said gasoline being substantially free from any tendency to deposit solids in aviation engine intake systems.

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