

1

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ANTICORROSIVE GASOLINE

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The present invention relates to corrosion inhibitors for gasolines having high octane ratings, and especially those gasolines designed for use in aircraft type internal combustion engines. More particularly, it relates to corrosion inhibitors formed as reaction products from alkyl acid phosphates and certain amines, and, which are compatible with other desirable additives. It further relates to anti-corrosive gasoline and means for producing the same. It also relates to the means for manufacturing corrosion inhibitors.

Recently, corrosion inhibitors for gasoline have attained importance as a result of research designed to inhibit corrosion in fuel systems and storage tanks, particularly where moist gasoline may come in contact with such metals as iron, copper, brass or the like. This type of corrosion is caused usually by the presence of water, and occurs generally at the water-gasoline interface. Furthermore, various components used in leaded gasolines are thought to be active promoters of corrosion.

The appearance of water as a separate phase in aviation gasoline may be caused either by entrained water from the fueling pumps used in fueling aircraft, since these use water displacement to pump the gasoline; or, by moisture in the air above the gasoline in the fuel tank, since, at temperatures prevalent in high altitude flying, the moisture condenses and precipitates.

Another class of important additives often used in aviation gasoline is composed of certain anti-knock agents designed particularly for rich mixture operation. Foremost among these additives are aniline and its homologs, such as for example, ethyl aniline, methyl aniline, amyl aniline, diamyl aniline, cumidine, and xylydine. These aromatic amines are very effective for this particular purpose when used in proportions of about one to three percent of the gasoline, and function as cumene substitutes in aviation gasoline blends.

Although corrosion inhibitors and the above mentioned anti-knock agents function excellently when each is used in the absence of the other, many of the common corrosion inhibitors are not compatible therewith. Consequently, when many of the alkyl acid phosphate-amine neutralization products conventionally used for anti-corrosion purposes are added to a gasoline containing aniline or a homolog of aniline, an undesirable precipitate or haze forms. The deleterious effects of precipitates in liquid fuels are well recognized, and in this instance they may form a stoppage in carburetor jets or other fine orifices as well as remove a substantial portion of the corrosion inhibitor from the gasoline solution. It will also be appreciated that gasoline homogeneity is one of the accepted requisites of marketability.

In accordance with the invention, it has been found that when alkyl acid phosphates are reacted, or neutralized, with branched chain dialkyl aliphatic amines having 4-15 carbon atoms per alkyl group and in which each branch is a methyl group attached to a carbon atom positioned at least two carbon atoms from the terminal carbon excellent gasoline soluble corrosion inhibitors are produced which

2

do not form precipitates or haze in gasoline solutions containing aniline or its homologs. Some examples of the aforesaid branched chain dialkyl aliphatic amines which are satisfactory for use in the present invention are suggested as follows:

Di secondary butylamine
Di secondary amylamine
Di 3-methyl pentylamine
Di 2,4-dimethyl hexylamine
Di 2,5,8 tri methyl dodecylamine

The need for methyl side chains in lieu of longer chains such as ethyl or propyl, for example, is confirmed by the fact that longer side chains do form precipitates when the reaction product therefrom is in the presence of aniline or its homologs. In this connection di 2-ethyl hexylamine is unsatisfactory for the reason stated above. Likewise, if the methyl group is attached to the next to the last carbon atom (i. e. in the so-called "iso" position) the compounds thus formed produce precipitates.

While certain variations and deviations from the teachings of the present invention are encompassed within its scope and spirit, it is nevertheless recommended that the process of manufacturing the finished gasolines containing desired additives be carried out in specified steps. For example, the order of addition of materials as well as the method of mixing the components must follow definite patterns.

The amine and alkyl acid phosphate may be reacted, or neutralized, by mixing the theoretical neutralizing quantities of the two components, heating above room temperature, care being taken not to exceed temperature at which decomposition takes place, and then thoroughly mixing until reaction is complete. The reaction product is tested to determine the degree of neutralization, and after neutralization is confirmed as complete, said reaction product is then blended into gasoline as desired, or may be blended into a small amount of gasoline to be used as a gasoline concentrate. The aniline or homolog thereof may be added in whatever order desired. However, the amine-alkyl acid phosphate neutralization product is insoluble in aniline and its homologs and as a consequence thereof a "one package" additive is not practical.

Another procedure for manufacturing the novel reaction products which inhibit corrosion comprises dissolving the amine or gasoline concentrate of amine in the gasoline to be treated, and then adding a predetermined amount of alkyl acid phosphate. Alternately, the alkyl acid phosphate may be added to the gasoline and then the required amount of amine added. The blend is then mixed thoroughly for about a half-hour to insure complete reaction. A similar procedure may be followed for the preparation of a gasoline concentrate, should this be desired. The blend or concentrate is then tested for degree of neutralization, and when found to be satisfactory as evidenced by its non-precipitation or non-haze formation, the aniline or its homolog, or a gasoline concentrate thereof, may then be added and the gasoline thoroughly mixed for ultimate use.

It is an important qualification of the present process that the aniline or homolog thereof never be mixed with a blend containing the alkyl acid phosphate until all of the acidity of the alkyl acid phosphate has been neutralized by the amine. To test the degree of neutralization, the following procedure has been found to be effective. A drop of the reaction mixture is added to a 1% solution of aniline in aviation gasoline. If precipitation occurs on mixing then a small additional quantity of the amine is added to the reaction mixture with continued heating and agitation. This procedure is followed until a non-precipitating reaction product is finally formed from

the alkyl acid phosphate and the branched chain dialkyl aliphatic amine.

The alkyl acid phosphates which may be used in the neutralization step of the present process are those having from 8 to 16 carbon atoms per alkyl group. Mainly for commercial reasons, the preferred alkyl acid phosphate is "Lorol" acid phosphate, which is a mixture of the phosphoric esters of "Lorol" alcohol. The term "Lorol" alcohol is used in the trade to denote a mixture of primary normal aliphatic alcohols of 8 to 12 carbon atoms which are obtained by fractionation of the alcohols resulting from the reduction of coconut and/or palm kernel oils. "Lorol" acid phosphate mixtures are readily obtainable on the market and for this reason are preferred to the more purified esters of greater scarcity and higher price. One "Lorol" acid phosphate is sold under the trade name "Ortholeum 162" and is understood to be mainly a mixture of mono and di acid phosphates of "Lorol" alcohol. Though for the reasons stated above "Lorol" acid phosphates are preferred, other alkyl acid phosphates containing from 8 to 16 carbon atoms per alkyl group are satisfactory. For example, a commercial grade of n-octyl acid phosphate was found to produce an excellent reaction product.

To form the desired neutralization product, the proper proportions of branched chain dialkyl aliphatic amine and alkyl acid phosphate may readily be determined by an electrometric titration of a sample of the alkyl acid phosphate with aqueous KOH solution to a pH of about 9. From the amount of KOH used the quantity of amine required to neutralize the acid radicals of the phosphate may easily be calculated. It is always desirable to have a slight excess of amine present, and good results have been obtained with as much as 50% excess of branched chain dialkyl aliphatic amine.

In order to prevent corrosion effectively, the lower concentration limit of the reaction product with respect to the finished gasoline should be about 0.002% by weight. This was determined by means of ASTM D665-47T corrosion test modified to a bath temperature of 80°-82° F. The upper concentration limit is determined by that amount of neutralization product which would cause engine deterioration due to the excessive quantity of phosphates then present. The upper limit is about 0.05% by weight.

Certain embodiments of the present invention are more fully illustrated by the following examples:

Example I

Into a suitable vessel equipped with means for heating, agitating, and cooling the charge, there are introduced 110 parts of di (secondary butyl) amine followed gradually by 150 parts of a mixture of mono and di "Lorol" acid phosphates (Ortholeum 162). The mixture is agitated vigorously and cooled as required to keep the temperature below 200° F. The reaction is vigorous and exothermic, consequently the rate of addition of the phosphate is controlled to avoid exceeding the above temperature limit. The resulting mixture is stirred for about 1 hour at 140° F. The reaction product is a viscous, oily liquid, yellow in color.

The reaction product is then tested for neutrality by means of the aforementioned neutralization test, and, if found to be acid, additional branched chain dialkyl aliphatic amine is added.

Finally, five pounds of the finished additive are added to 17,000 gallons of aviation gasoline in a blender and agitated for about 15 minutes. Then 1020 pounds of mixed xylinides are added and the mixture resulting therefrom is agitated for about a half-hour. The final gasoline is completely homogeneous, free from haze, corrosion-resistant, and has a rich mixture anti-knock rating commensurate with the amount of xylinides used.

Example II

A 10% by weight solution in gasoline of the finished additive from Example I is prepared by dissolving 100 pounds of the reaction product in 900 pounds of gasoline in a mixer. The gasoline-additive concentrate is thoroughly mixed for about one hour, and 50 pounds of this concentrate then blended into 17,000 gallons of aviation gasoline. The resulting mixture is agitated for about 15 minutes. Finally, 1020 pounds of mixed xylinides are added and mixing continued for an additional 30 minutes. This finished product is comparable to that obtained in Example I.

Example III

To 17,000 gallons of aviation gasoline in a blender are added 7.10 lbs. of di (2,5,8-trimethyl dodecyl) amine. The resulting mixture is thoroughly agitated for about 10 minutes, and then 2.68 pounds of a mixture of mono and di "Lorol" acid phosphate (Ortholeum 162) are added with continued mixing for about one-half hour. After the neutralization tests indicate the production of a satisfactory reaction product, 1020 pounds of mono methyl aniline are added and agitation continued for another half-hour. As in the former examples, tests indicate the production of excellent quality finished gasoline.

Example IV

To 17,000 gallons of aviation gasoline in a blender are added 3.00 pounds of di (3-methyl pentyl) amine. The resulting mixture is thoroughly agitated for about 10 minutes, and then 2.68 pounds of a mixture of mono and di "Lorol" acid phosphate (Ortholeum 162) are added with continued mixing for about one-half hour. After the neutralization tests indicate the production of a satisfactory reaction product, 1020 pounds of mono methyl aniline are added and agitation continued for another half-hour. As in the former examples tests indicate the production of excellent quality finished gasoline.

Although aviation gasolines are used in the above examples for purposes of illustration, and such gasolines may comprise the following:

Alkylate	percent	70-88
Aromatics	do	5-16
Isopentane	do	5-14
Tetra ethyl lead	cc. per gallon	4

nevertheless, the invention in its broadest scope comprehends the treatment of any motor fuel. Similarly, it will be appreciated that the reaction product of the present invention may be blended in proper proportions in any desired gasoline with the advantage that the purchaser or user may add any suitable amount of aniline or homologs thereof, for the purpose of obtaining rich mixture anti-knock properties, without difficulties arising from precipitation of haze formation which is generally encountered when less satisfactory corrosion inhibitors are used.

It will now be apparent that I have devised a novel and useful process and composition of matter which embodies the features of advantage enumerated as desirable in the statement of the invention and the above description and while in the present instance there are described the preferred embodiments thereof which have been found in practice to give satisfactory and reliable results, it is to be understood that the same is susceptible of modification in various particulars without departing from the spirit or scope of the invention or sacrificing any of its advantages.

I claim:

1. A completely homogeneous, corrosion-resistant aviation fuel having a high rich mixture anti-knock rating, comprising gasoline containing sufficient aromatic amine from the group consisting of aniline and homologs of aniline to substantially increase the rich mixture anti-knock properties of the gasoline and between 0.002% and

5

0.05% by weight of the finished gasoline of the addition product resulting from contacting an alkyl acid phosphate having from 8 to 16 carbon atoms per alkyl group with between 100% and 150% of the quantity theoretically required to neutralize said phosphate of a branched chain dialkyl aliphatic amine having 4-15 carbon atoms per alkyl group and in which each branch is a methyl group attached to a carbon atom positioned at least two carbon atoms from the terminal carbon.

2. An anti-corrosive gasoline as in claim 1 wherein the branched chain dialkyl aliphatic amine is di (secondary butyl) amine.

3. An anti-corrosive gasoline as in claim 1 wherein the branched chain dialkyl aliphatic amine is di (2,5,8-trimethyl dodecyl) amine.

4. An anti-corrosive gasoline as in claim 1 wherein the branched chain dialkyl aliphatic amine is di (3-methyl pentyl) amine.

5. The method of simultaneously improving the anti-corrosive and the rich mixture anti-knock properties of a gasoline, which comprises forming in said gasoline a corrosion inhibiting amount of the addition product of an alkyl acid phosphate having 8 to 16 carbon atoms per alkyl group and a branched chain dialkyl aliphatic amine having 4-15 carbon atoms per alkyl group and in which each branch is a methyl group attached to a carbon atom positioned at least two carbon atoms from the terminal carbon and in which all the acid hydrogen of said phosphate is neutralized by said amine, then adding sufficient aromatic amine from the group consisting of aniline and homologs of aniline to substantially increase the rich mixture anti-knock properties.

6

6. The method of inhibiting the formation of an insoluble precipitate when an amine-phosphate corrosion inhibitor is added to a gasoline containing an aniline octane booster, which comprises adding to a gasoline an alkyl acid phosphate having 8 to 16 carbon atoms per alkyl group, adding between 100% and about 150% of the quantity theoretically required to neutralize all the acid hydrogen of said phosphate of a branched chain dialkyl aliphatic amine having 4-15 carbon atoms per alkyl group and in which each branch is a methyl group attached to a carbon atom positioned at least two carbon atoms from the terminal carbon thereby forming in said gasoline an addition product of said amine with said phosphate, then adding sufficient aromatic amine from the group consisting of aniline and homologs of aniline to substantially increase the rich mixture anti-knock properties of the gasoline, the amounts of the amine and the phosphate being such as to produce an addition product of between 0.002% and 0.05% by weight of the finished gasoline.

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