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 the 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, dimethyl aniline, cumidine, and xyldine. 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 cumin substitutes in aviation gasoline blends.

Although corrosion inhibitors and octane improvers function excellently when each is used in the absence of the other, many of the common corrosion inhibitors are not compatible with the aforesaid rich mixture anti-knock boosters. Consequently, when many of the alkyl acid phosphate—amine neutralization products 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 certain specific amines hereinafter enumerated excellent gasoline soluble corrosion inhibitors are produced which do not form precipitates or haze in gasoline solutions containing aniline or its homologs.

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, and then removing the excess amine by conventional means to obtain a solution which on standing forms no precipitate or haze in gasoline solution. The reaction mixture is then readjusted to the proper neutralization point by adding an excess of the other component. The reaction product is then filtered to remove any insoluble material which may form during reaction.

Another step of the invention consists in the addition of a corrosion inhibitor to gasoline containing aniline or its homologs. The corrosion inhibitor is added either to the gasoline containing aniline or its homologs or to the mixture of components after the reaction is complete. The method of neutralization is not limited to the specific steps outlined above. Other methods of neutralization may be used without departing from the spirit of the invention. The addition of the corrosion inhibitor is usually carried out at the refinery where the gasolines are prepared, or in the distribution plants or at the point of sale. While the corrosion inhibitor is preferably added to the gasoline containing the amine, it may also be added to the gasoline before the amine is added. The corrosion inhibitor is usually added in amounts of from 0.1 to 1.0 weight percent of the gasoline.

The invention is applicable to all gasolines containing from 8 to 16 carbon atoms per alkyl group, and is especially applicable to gasolines containing from 8 to 12 carbon atoms per alkyl group.
acid phosphate was found to produce an excellent reaction product. The excellent quality gasolines which may be produced by the present process comprise products resulting from reaction of the aforementioned alkyl acid phosphates with the branched alkyl amine of four or more carbon atoms and having no more than two carbon atoms in any one side chain. Examples of these amines are as follows: iso amyl amine, 1 methyl propyl amine, 2 amino 4 methyl pentane, 2 amino octane, 2 ethyl hexyl amine, 3,5,5, tri methyl hexahexylamine, 1,1,3,3, tetramethyl butylamine, iso butyl amine, reaction butylamine, mixed branched chain octadeclamylines (such as those marketed by Rohm & Haas under the trade name “Alkyamine JM-R”), and mixed branched chain 12-15 carbon atom alkyl amines (such as those marketed by Rohm & Haas under the trade name “Alkyamine 81-R”).

To form the desired neutralization product, the proper proportions of 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 be easily 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 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 D663-47T 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. This 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 122 parts of 3,5,5 tri methyl hexahexylamine followed gradually by 150 parts of a mixture of mono and di “Lorol” acid phosphates (Orthoelum 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 specified 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.

This reaction product is then tested for suitability as an additive for aviation gasolines containing aniline or homologs thereof by means of the aforementioned neutralization test. 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 product is complete homogeneous, free from haze, corrosion resistant, and has a high 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 those obtained in Example I.

**Example III**

To 17,000 gallons of aviation gasoline in a blender are added 2,52 pounds of 3,5,5 tri methyl hexyl 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 (Orthoelum 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 amine is added and agitation continued for another half-hour. As in the former examples, tests indicate the production of excellent quality finished gasoline.

**Example IV**

The same procedure is used as in Example I except that 62 parts of 1 methyl propyl amine are introduced into the vessel in lieu of 122 parts of 3,5,5 tri methyl hexahexylamine and 1500 pounds of methyl aniline are used instead of the mixed xylinides.

**Example V**

The same procedure is used as in Example I except that 62 parts of 1 methyl propyl amine are introduced into the vessel in lieu of above acid phosphates of 3,5,5 trimethyl hexahexylamine, and 3000 pounds of methyl aniline are used instead of the mixed xylinides.

**Example VI**

The same procedure is used as in Example I except that 110 parts of 2 ethyl hexylamine are introduced into the vessel in lieu of 122 parts of 3,5,5 trimethyl hexylamine.

**Example VII**

The same procedure is used as in Example I except that 86 parts of 2 amino 4 methyl pentane are introduced into the vessel in lieu of 122 parts of 3,5,5 trimethyl hexahexylamine.

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

<table>
<thead>
<tr>
<th>Component</th>
<th>Percent</th>
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<tbody>
<tr>
<td>Alkylate</td>
<td>70-88</td>
</tr>
<tr>
<td>Aromatics</td>
<td>5-16</td>
</tr>
<tr>
<td>Tetraethyl lead</td>
<td>5-14</td>
</tr>
<tr>
<td>No.2 gasoline</td>
<td>4 cc per gallon</td>
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</tbody>
</table>

nevertheless, the invention in its broadest scope comprehends the treatment of aviation fuels. It will be appreciated that the reaction product of the present invention may be blended in proper proportions in a desired aviation gasoline with the advantage that the purchaser or user may add any suitable amount of aniline or homologs thereof, for the purpose of obtaining desirable rich mixture anti-knock properties, without difficulties arising from precipitation or 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 a 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 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 mono alkyl mono amine having at least four carbon atoms, and less than three carbon atoms in any one side chain.

2. An anti-corrosive gasoline as in claim 1 wherein the amine is 3,5,5 trimethyl hexylamine.

3. An anti-corrosive gasoline as in claim 1 wherein the amine is 1,1,3,3 tetramethyl butylamine.

4. An anti-corrosive gasoline as in claim 1 wherein the amine is 1 methyl propyl amine.

5. An anti-corrosive gasoline as in claim 1 wherein the amine is 2 ethyl hexylamine.

6. An anti-corrosive gasoline as in claim 1 wherein the amine is 2 amino 4 methyl pentane.

7. 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 said phosphate of a branched chain mono alkyl mono amine having at least four carbon atoms and less than three carbon atoms per side chain, agitating the mixture until neutralization is complete while holding the temperature above room temperature and below 200° F., 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 sufficient to produce an addition product of between 0.002% and 0.05% by weight of the finished gasoline.

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