The present invention relates to a method of stabilizing organic compounds, and particularly to the stabilization of organic substances against deterioration by oxygen catalyzed in the presence of or by contact with certain oxidation promoters.

While the present invention is applicable to preventing such deterioration of fats, resins, rubber, etc., it is particularly applicable to the stabilization of olefin-containing hydrocarbon distillates, such as cracked or polymer gasolines.

One method of refining gasoline is the copper sweetening process, in which the use of the gasoline is contacted with a copper-containing catalyst. As a result of this treatment, the sweetened gasoline usually contains relatively small amounts of copper compounds which have a catalytic effect on oxidation reactions resulting when the gasoline comes in contact with air. In addition, gasolines come in contact with various metals in the course of refining, storing and shipping operations, and the metal may catalyze the oxidation reactions. In some cases, this may also result in the gasoline containing minor amounts of such metals as copper, iron, cobalt, nickel, chromium, lead, etc., which have a detrimental effect on the stabilization of the gasoline.

In a broad aspect, the present invention relates to a method of stabilizing an organic substance subject to oxidative deterioration in the presence of a metal or its compounds which normally catalyzes said deterioration, which comprises adding thereto a metal deactivator comprising a mixture of at least two salicylalaminophenols.

In still another specific embodiment, the metal deactivator of the present invention may comprise a mixture of at least two salicylalaminophenols whose alkyl groups are different.

In another embodiment of the invention, the metal deactivator may comprise a mixture of two or more of the various alkyl substituted ortho-amino-phenols hereinbefore set forth. In other words, the unsubstituted 2-salicylalaminophenol need not necessarily be present.

While 2-salicylalaminophenol is a satisfactory deactivator, it is not sufficiently soluble in cracked gasoline to permit its use with gasolines containing increased amounts of metal compounds. One method of increasing the solubility of the metal deactivator in gasoline is the use of an external solvent, such as ether, alcohol, ester, etc., but it has been found that the deactivator is not sufficiently soluble in readily available inexpensive solvents and it may be necessary to resort to the use of more expensive solvents. This is objectionable since it may increase the cost of the product to an exorbitant extent.

I have now found that a mixture of suitably substituted salicylalaminophenols improves the solubility of the deactivator, with the result that the deactivator will not crystallize out of solution at the low temperatures sometimes encountered in the use of gasoline. In addition to this important advantage, the mixed deactivators of the present invention are of unexpectedly higher potency.

In one embodiment of the invention, the mixed metal deactivator may comprise 2-salicylalaminophenol in admixture with one or more of the following: 2-salicylalaminophenol - 4-ethylphenol, 2-salicylalaminophenol - 4-normal propylphenol, 2-salicylalaminophenol - 4-isopropylphenol, 2-salicylalaminophenol - 4-normal butylphenol, 2-salicylalaminophenol - 4-sec-butylphenol, 2-salicylalaminophenol - 4-ter-butylphenol, 2-salicylalaminophenol - 4-normal amylphenol, 2-salicylalaminophenol - 4-isoamylphenol, 2-salicylalaminophenol - 4-sec-amylphenol, 2-salicylalaminophenol - 4-ter-amylphenol, 2-salicylalaminophenol - 4-normal hexylphenol, 2-salicylalaminophenol - 4-iso-hexylphenol, 2-salicylalaminophenol - 4-sec-hexylphenol, 2-salicylalaminophenol - 4-ter-hexylphenol, 2-salicylalaminophenol - 4-normal heptylphenol, 2-salicylalaminophenol - 4-iso-heptylphenol, 2-salicylalaminophenol - 4-sec-heptylphenol, 2-salicylalaminophenol - 4-ter-heptylphenol, 2-salicylalaminophenol - 4-normal octylphenol, 2-salicylalaminophenol - 4-iso-octylphenol, 2-salicylalaminophenol - 4-sec-octylphenol, 2-salicylalaminophenol - 4-ter-octylphenol, etc.

While the preferred compounds comprise those in which the alkyl group is positioned para to the hydroxy group (alkyl group being in the four position), it is understood that the alkyl groups may be located at different positions on the ring, and also that two or more alkyl groups may be attached to one or both of the rings. It is further understood that, in some cases, other hydrocarbon groups such as phenyl, cyclohexyl, alkoxyphenyl, alklycyclohexyl, may be attached to one or both of the rings in place or in addition to the alkyl groups. It is still further understood that the various mixed metal deactivators which may be prepared and utilized in the broad scope of the present invention will not necessarily be equivalent.

In general, it is preferred that the various substituents be substantially different, in order to avoid any possible isomorphous crystallization, which may occur when similar substituent groups are present.

The improved metal deactivator of the present invention may be prepared by forming the various components separately and then blending either the pure compounds or solutions thereof, or the mixed deactivator may be prepared in one operation by mixing the different orthoaminophenols and coupling them with salicylaldehyde, in one step. In general, the metal deactivator of the present invention may be made by first forming separate alcoholic solutions of salicylaldehyde and of one or more orthoaminophenols. The alcohol solutions may then be mixed and the
mixture warmed. The product is purified by recrystallization.

Another advantage to the metal deactivator of the present invention is that it is completely compatible with known oxidation and gum inhibitors which are added to gasoline to minimize or prevent deleterious oxidation reactions which form gum and other undesirable products. Well known inhibitors include various phenolic, amino, and aminophenolic compounds, as well as fractions of wood tar oil, etc., and are usually added to gasoline in concentrations of 0.001% to 0.1% by weight. Some of these inhibitors are marketed in the form of a solution in a suitable solvent, such as alcohol, ether, etc., and in most cases the solvent for the inhibitor may also function as the solvent for the metal deactivator of the present invention. In one embodiment of the invention, the inhibitor and the metal deactivator may be prepared as a mixture in a solvent, and the combined inhibitor and deactivator may be marketed as a single commodity of two-fold purpose.

In another embodiment of the invention, the metal deactivator may be marketed as such or may be dissolved in a suitable solvent and the solution marketed. Any suitable solvent may be employed including alcohols, such as methyl alcohol, ethyl alcohol, isopropyl alcohol, sec-butyl alcohol, etc., various ethers and esters, hydrocarbons such as benzene, xylene, etc., or mixtures of these various solvents. The metal deactivator of the present invention has a tendency to react with solvents such as acetone and furfural and for this reason the use of these solvents is not preferred because of the resulting reduction in effectiveness after long periods of time. Pyridine is a nitrogen base and therefore is not particularly desirable as an additive to motor fuel and further it is relatively expensive. It therefore is not generally desirable as a solvent for the present purpose. An alcohol or ether solvent is particularly preferred, both because of their cheap cost and ready availability and also because they do not adversely affect the metal deactivator.

The metal deactivator of the present invention may be used in gasoline in amounts of about 0.0001% to about 0.01% and may be added to the gasoline as such, in a suitable solvent, or in any suitable mixture with the oxidation inhibitor, in the manner hereinabove set forth.

It is understood that the metal deactivators of the present invention are generally utilized in addition to the oxidation inhibitors hereinbefore set forth and that the function of the metal deactivator is entirely distinct from the function of the inhibitor. For example, the oxidation inhibitor does not suppress the catalytic action of the metal to any considerable extent and, on the other hand, the metal deactivator does not suppress oxidation reactions per se, to any considerable extent but serves only to deactivate the metal compounds and thereby destroy the catalytic effect thereof to enhance oxidation reactions.

The following examples are introduced to illustrate further the novelty and utility of the present invention but not with the intention of unduly limiting the same.

EXAMPLE I

The following example shows the temperature of crystallization of (1) 2-salicylamidophenol, (2) 2-salicylamino-4-ter-amylyphenol, (3) 2-salicylamino-4-sec-butylyphenol, and (4) 2-salicylamino-4-ethyllyphenol, in comparison with (5) a mixture of 15% 2-salicylamidophenol and 85% 2-salicylamino-4-ter-amylyphenol, (6) a mixture of 10% 2-salicylamidophenol, 45% 2-salicylamino-4-ter-amylyphenol, and 45% 2-salicylamino-4-sec-butylyphenol, and (7) a mixture of 15% 2-salicylamidophenol, 65% 2-salicylamino-4-ter-amylyphenol and 20% 2-salicylamino-4-ethyllyphenol.

After being separately prepared, all of the above metal deactivators were dissolved in separate portions of anhydrous sec-buty-alcohol solvent. The amount of metal deactivator in the solvent is indicated in the following table:

<table>
<thead>
<tr>
<th>Deactivator</th>
<th>Percent by Weight in Solvent</th>
<th>Temperature of Crystallization, °F.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) 2-salicylamidophenol</td>
<td>15</td>
<td>45</td>
</tr>
<tr>
<td>(2) 2-salicylamino-4-ter-amylyphenol</td>
<td>30</td>
<td>40</td>
</tr>
<tr>
<td>(3) 2-salicylamino-4-sec-butylyphenol</td>
<td>25</td>
<td>32</td>
</tr>
<tr>
<td>(4) 2-salicylamino-4-ethyllyphenol</td>
<td>25</td>
<td>40</td>
</tr>
<tr>
<td>(5) Mixture of 15% 2-salicylamidophenol and 85% 2-salicylamino-4-ter-amylyphenol</td>
<td>30</td>
<td>0</td>
</tr>
<tr>
<td>(6) Mixture of 15% 2-salicylamidophenol, 45% 2-salicylamino-4-ter-amylyphenol, and 40% 2-salicylamino-4-sec-butylyphenol</td>
<td>30</td>
<td>0</td>
</tr>
<tr>
<td>(7) Mixture of 15% 2-salicylamidophenol, 65% 2-salicylamino-4-ter-amylyphenol, and 20% 2-salicylamino-4-ethyllyphenol</td>
<td>30</td>
<td>Less than 10</td>
</tr>
</tbody>
</table>

It is apparent from the above data that the temperature of crystallization of the mixed deactivators is considerably lower, and therefore that no difficulty in commercial use should be encountered, particularly with the three component mixture comprising 2-salicylamidophenol, 2-salicylamino-4-ter-amylyphenol, and 2-salicylamino-4-ethyllyphenol.

EXAMPLE II

As heretoforementioned, the potency of the mixed metal deactivators is higher than that of the single compounds and this is illustrated in Table II. In this series of tests, some of the metal deactivator solutions specified in Example I were added to Pennsylvania thermally cracked gasoline in an amount of 0.0097% by weight. In addition, 0.01% of an inhibitor comprising a major proportion of an aminophenol and a minor proportion of a phenylene diamine was added to the gasoline. 1 mg. of copper per liter was also added, and the induction periods obtained on the various samples are given below.

The induction period of the inhibited gasoline without added copper was 570 minutes.

<table>
<thead>
<tr>
<th>Metal Deactivator</th>
<th>Induction Period, Minutes</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-salicylamino-4-ter-amylyphenol</td>
<td>375</td>
</tr>
<tr>
<td>Mixture of 15% 2-salicylamidophenol and 85% 2-salicylamino-4-ter-amylyphenol</td>
<td>405</td>
</tr>
<tr>
<td>Mixture of 15% 2-salicylamidophenol, 45% 2-salicylamino-4-ter-amylyphenol, and 20% 2-salicylamino-4-ethyllyphenol</td>
<td>455</td>
</tr>
</tbody>
</table>

In the absence of any metal deactivator, the induction period of the inhibited gasoline fell
to 200 minutes upon the addition of 1 mg. of copper per liter.

**Example III**

In another series of tests, similar to Example I, but using ethyl acetate as the solvent, the following temperatures of crystallization were determined:

**Table III**

| Deactivator | Per cent. by weight in solvent | Temperature of crystallization, °F.
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>2-salicylamino-4-sec-butylphenol</td>
<td>40</td>
<td>15</td>
</tr>
<tr>
<td>2-salicylamino-4-ter-ethylphenol</td>
<td>40</td>
<td>10</td>
</tr>
<tr>
<td>Mixture of 10% 2-salicylamino-phenol, 45% 2-salicylamino-4-ter-amylphenol, and 45% 2-salicylamino-4-ter-butylphenol</td>
<td>40</td>
<td>0</td>
</tr>
<tr>
<td>Mixture of 10% 2-salicylamino-phenol, 60% 2-salicylamino-4-ter-amylphenol, and 20% 2-salicylamino-4-ethylphenol</td>
<td>40</td>
<td>Less than 5</td>
</tr>
</tbody>
</table>

**EXAMPLE IV**

In another series of tests, separate solutions were prepared of various metal deactivators in 89 octane all-purpose gasoline comprising a mixture of cracked and straight-run gasolines. The various metal deactivators solutions were as follows: (1) a solution of 0.5% by weight of 2-salicylamino-4-tetramethylphenol, (2) a solution of 0.5% by weight of 2-salicylamino-4-sec-butylphenol, (3) a solution of 0.5% by weight of a mixture of 10% 2-salicylamino-phenol, 45% 2-salicylamino-4-ter-amylphenol, and 45% 2-salicylamino-4-ter-butylphenol, (4) a solution of 0.5% by weight of a mixture of 15% 2-salicylamino-phenol, 65% 2-salicylamino-4-ter-amylphenol, and 20% 2-salicylamino-4-ethylphenol. These solutions were stored at 8°F. and after 2 to 3 hours the solution of 2-salicylamino-4-ter-amylphenol and the solution of 2-salicylamino-4-sec-butylphenol became crystallized, but the other two solutions comprising the mixed metal deactivators did not crystallize after storage at 8°F.

I claim as my invention:

1. A method of stabilizing olefinic gasoline subject to oxidative deterioration in the presence of a metal which normally catalyzes said deterioration, which comprises adding thereto a metal deactivator comprising a mixture of 2-salicylamino-phenol and a 2-salicylamino-alkylphenol.

2. The process of claim 1 further characterized in that said deactivator comprises a mixture of 2-salicylamino-phenol and at least two 2-salicylamino-alkylphenols, in which the alkyl groups are different.

3. The method of stabilizing gasoline containing unsaturated hydrocarbons which tend to form gums and containing a metal which normally catalyzes oxidative deterioration, which comprises adding to said gasoline an inhibitor to prevent said gum formation and a smaller amount of a metal deactivator comprising a mixture of 2-salicylamino-phenol and a 2-salicylamino-alkylphenol.

4. The process of claim 3 further characterized in that said mixture comprises 2-salicylamino-phenol and a 2-salicylamino-4-alkylphenol.

5. The process of claim 3 further characterized in that said mixture comprises 2-salicylamino-phenol and at least two 2-salicylamino-4-alkylphenols in which the alkyl groups are different.

6. Olefinic gasoline subject to oxidative deterioration in the presence of a metal which normally catalyzes said deterioration containing as a deactivator of the catalytic effect of said metal, a mixture of 2-salicylamino-phenol and a 2-salicylamino-alkylphenol.

7. The composition of claim 6 further characterized in that said mixture comprises 2-salicylamino-phenol and 2-salicylamino-4-alkylphenol.

8. The composition of claim 6 further characterized in that said mixture comprises 2-salicylamino-phenol and at least two 2-salicylamino-4-alkylphenols in which the alkyl groups are different.


10. A mixture of 2-salicylamino-phenol and 2-salicylamino-4-alkylphenol.

11. A mixture of 2-salicylamino-phenol at least two 2-salicylamino-4-alkylphenols in which the alkyl groups are different.

12. A method of stabilizing olefinic gasoline subject to oxidative deterioration in the presence of a metal which normally catalyzes said deterioration, which comprises adding thereto a metal deactivator comprising a mixture of 2-salicylamino-phenol and a 2-salicylamino-4-alkylphenol wherein the alkyl radical contains from 1 to 8 carbon atoms.

13. The method of stabilizing gasoline containing unsaturated hydrocarbons which tend to form gums and containing a metal which normally catalyzes oxidative deterioration, which comprises adding to said gasoline an inhibitor to prevent said gum formation and a smaller amount of a metal deactivator comprising a mixture of 2-salicylamino-phenol and a 2-salicylamino-4-alkylphenol wherein the alkyl radical contains from 1 to 8 carbon atoms.

14. Olefinic gasoline subject to oxidative deterioration in the presence of a metal which normally catalyzes said deterioration containing as a deactivator of the catalytic effect of said metal, a mixture of 2-salicylamino-phenol and a 2-salicylamino-4-alkylphenol wherein the alkyl radial contains from 1 to 8 carbon atoms.

15. A mixture of 2-salicylamino-phenol and a 2-salicylamino-4-alkylphenol wherein the alkyl radical contains from 1 to 8 carbon atoms.

16. The method of stabilizing gasoline containing unsaturated hydrocarbons which tend to form gums and containing a metal which normally catalyzes oxidative deterioration, which comprises adding to said gasoline an inhibitor to prevent said gum formation and a smaller amount of a metal deactivator comprising a mixture of 2-salicylamino-phenol, 2-salicylamino-4-ter-amylphenol, and 2-salicylamino-4-ethylphenol.

17. Olefinic gasoline subject to oxidative deterioration in the presence of a metal which normally catalyzes said deterioration containing as a deactivator of the catalytic effect of said metal, a mixture of 2-salicylamino-phenol, 2-salicylamino-4-ter-amylphenol, and 2-salicylamino-4-ethylphenol.

RALPH B. THOMPSON.

REFERENCES CITED

The following references are of record in the file of this patent:

**UNITED STATES PATENTS**

<table>
<thead>
<tr>
<th>Number</th>
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<tr>
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<td>Chemuck</td>
<td>July 15, 1941</td>
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