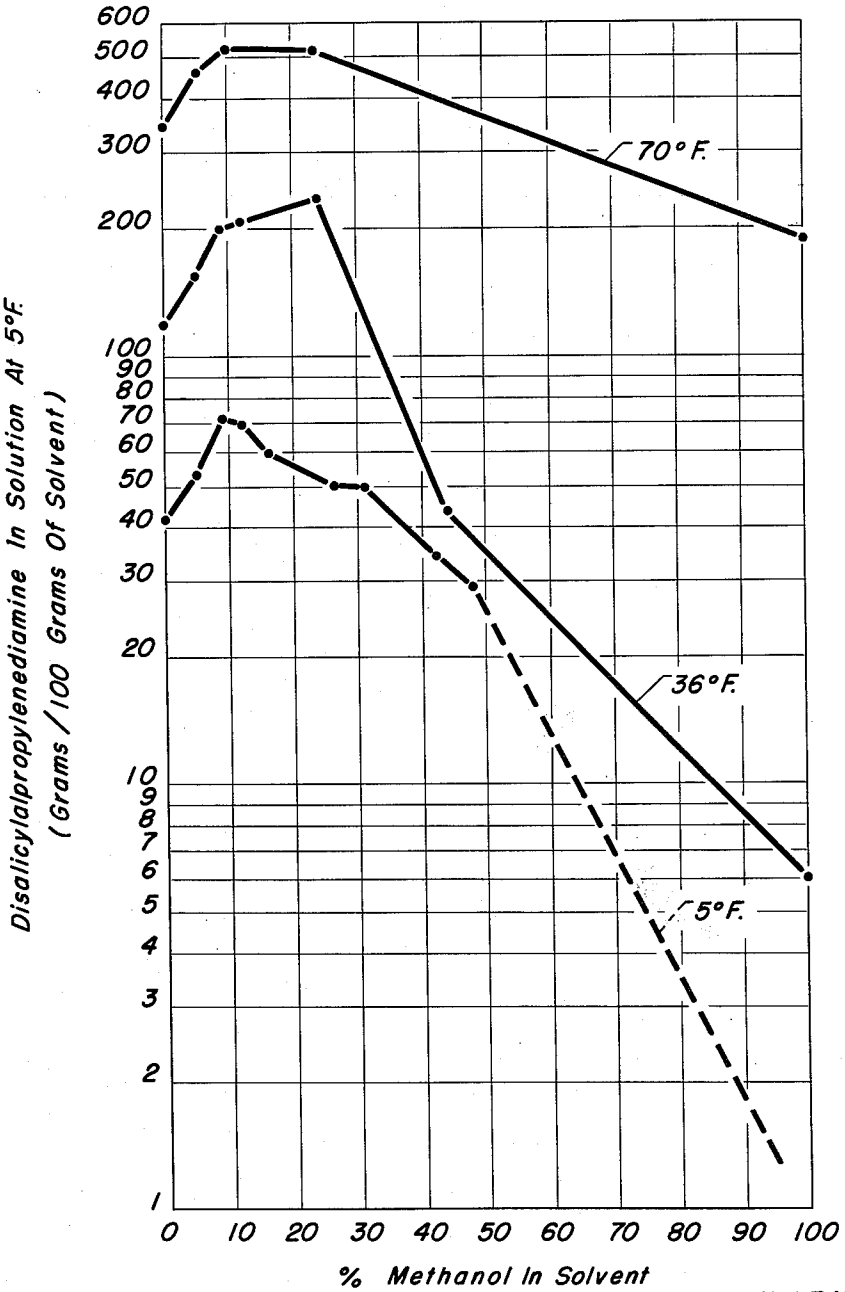
July 10, 1962 J. P. HATCHER ET AL 3,043,783

METAL DEACTIVATOR COMPOSITION OF LOW FREEZING PROPERTIES

Filed March 31, 1960



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United States Patent Office

3,043,783

Patented July 10, 1962

3,043,783

METAL DEACTIVATOR COMPOSITION OF LOW FREEZING PROPERTIES

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Filed Mar. 31, 1960, Ser. No. 18,918
2 Claims. (Cl. 252—403)

This is a continuation-in-part of application Serial No. 717,847, filed February 27, 1958, now abandoned, which in turn is a continuation-in-part of application Serial No. 602,496, filed August 7, 1956, now abandoned, and relates to a novel metal deactivator composition of low freezing properties.

A major disadvantage to certain metal deactivators being marketed at the present time is that the metal deactivators are not sufficiently soluble in the commonly used solvents at low temperatures. Accordingly, during the winter months the active component of the metal deactivator precipitates out of solution and freezes in the drums, tanks or other receptacles, and the metal deactivator cannot be pumped or used in the normal manner. It is apparent that this is a serious disadvantage and entails additional expense and time on the part of the user in order to warm the solution to a suitable temperature at which it can be pumped.

It now has been found that a mixed solvent solution containing critical proportions of the components will provide a solution which will remain liquid at these low temperatures. As will be shown by the appended examples, the novel mixed solvent of the present invention results in a solution which will remain liquid at lower temperatures than is obtainable by using either of these solvent components separately. Accordingly, the novel solution of the present invention can be pumped and used as required without the necessity of heating and other handling before satisfactory use of the metal deactivator.

The novel metal deactivator composition of the present invention is employed to deactivate the catalytic effect of metals in any substrate containing such metals. These metals catalyze oxidation of organic substances. The metal deactivator composition thus is useful to prevent such deterioration of motor fuels, fats, edible oils, lubricating oils, diesel oils, fuel oils, etc. The present invention is particularly applicable to the stabilization of olefin-containing motor fuels such as cracked or polymer gasoline, or mixtures of these with straight run and/or natural gasolines.

One method of refining gasoline is the copper sweetening process, in which process the gasoline is treated with a copper-containing reagent. As a result of this treatment, the sweetened gasoline usually contains relatively small amounts of copper compounds which catalyze oxidation reactions. In addition, gasolines come in contact with various metals in the course of refining, storing and shipping operations, and the metals may catalyze the oxidation reactions. In some cases, this also may 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 stability of the gasoline. In addition to gasoline, the other organic compounds hereinbefore set forth also become contaminated with metallic constituents during the course of refining, storing

and shipping operations and, accordingly, are deleteriously affected by the metallic constituents.

A particularly effective metal deactivator comprises the condensation product of an ortho-hydroxy aromatic aldehyde with an aliphatic amine. For example, disalicylalpropylenediamine is prepared by the condensation of 2 mols of salicylaldehyde with 1 mol of propylenediamine. For ease in handling and use, the disalicylalpropylenediamine is prepared as a solution in an aromatic solvent. While this metal deactivator composition is very effective, it suffers from the disadvantage of having too high a freezing point. For example, at temperatures normally encountered in the winter months, disalicylalpropylenediamine precipitates out of solution. This interferes with the easy use of the deactivator composition and necessitates heating of the composition in order to dissolve the disalicylalpropylenediamine in the solvent. This disadvantage is avoided by the novel metal deactivator composition of the present invention.

In one embodiment the present invention relates to a metal deactivator composition comprising the condensation product of an ortho-hydroxy aromatic aldehyde with an aliphatic amine dissolved in a solvent mixture of from about 5% to about 25% by weight of an alcohol and from about 95% to about 75% by weight of an aromatic hydrocarbon.

In a specific embodiment the present invention relates to a metal deactivator composition comprising from about 30% to about 80% and more particularly from about 40% to about 60% by weight of the condensation product of salicylaldehyde with propylenediamine dissolved in from about 20% to about 70% and more particularly from about 40% to about 60% by weight of a solvent mixture containing from about 5% to about 25% by weight of methanol and from about 75% to about 95% by weight of toluene.

In another embodiment the present invention relates to an organic substance containing a metal which normally catalyzes oxidative deterioration and additionally containing a small amount of the metal deactivator composition set forth herein.

As hereinbefore set forth, the metal deactivator composition includes the condensation product of an ortho-hydroxy aromatic aldehyde with an aliphatic amine. Any suitable ortho-hydroxy aromatic aldehyde may be utilized and preferably comprises salicylaldehyde or ortho-vanillin and mixtures thereof. Other ortho-hydroxy aromatic aldehydes include 2-hydroxy-6-methyl-benzaldehyde, 2-hydroxy-3-methoxy-benzaldehyde, 2-hydroxy-4-methoxy-benzaldehyde, 2,4-dihydroxy-benzaldehyde, 2,6-dihydroxy-benzaldehyde, 2-hydroxy-naphthaldehyde-1, 1-hydroxy-naphthaldehyde-2, anthrol-2-aldehyde-1, etc., or mixtures thereof. It is understood that the various ortho-hydroxy aromatic aldehydes are not necessarily equivalent and that the specific ortho-hydroxy-aromatic aldehyde used will be selected with reference to its effectiveness, availability and cost.

Any suitable aliphatic amine is condensed with the ortho-hydroxy aromatic aldehyde. Alkylene polyamines are preferred and thus include ethylenediamine, propylenediamine, 1,3-diaminopropane, 1,2-diaminobutane, 2,3-diaminobutane, diethylenetriamine, dipropylenetriamine, triethylenetetramine, etc., or mixtures thereof. It is understood that the aliphatic amines are not necessarily equivalent and, likewise, that the specific amine to be

used will be selected with reference to its effectiveness, availability and cost.

When either two or more ortho-hydroxy aromatic aldehydes and/or two or more aliphatic amines are used in the preparation of the metal deactivator, the metal deactivator will comprise a mixture of the condensation products. This mixture is referred to herein as active ingredient, in contrast to the solvent which is not active to effect deactivation of metals.

The condensation of ortho-hydroxy aromatic aldehyde and aliphatic amine is effected in any suitable manner. The reaction is effected readily at room temperature and generally is effected in the presence of an organic solvent in order to facilitate subsequent removal of the water formed in the reaction. Water and solvent are removed in any suitable manner, including draining, distillation, etc.

As hereinbefore set forth, the condensation product is prepared as a solution in a particular mixed solvent. Also, as hereinbefore set forth, the mixed solvent of the present invention results in a solution which remains liquid at lower temperatures than solutions containing either one of the solvents alone. The preferred mixed solvent of the present invention comprises from about 5% to about 25% by weight of methanol and from about 75% to about 95% by weight of toluene.

While the mixture of methanol and toluene is particularly preferred, in some cases other aromatic hydrocarbons and other alcohols may be used. Other aromatic hydrocarbons include benzene, xylene, cumene, etc. or mixtures thereof and/or with toluene. Other alcohols include ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol and, in some cases, pentanol, hexanol, heptanol, octanol, etc., or mixtures of these and/or mixtures thereof with methanol. However, it is understood that the different aromatic hydrocarbons and alcohols are not necessarily equivalent.

As hereinbefore set forth, the mixed solvent of the present invention provides a metal deactivator composition of improved solidification properties. These improved properties result in a solution which will remain liquid at lower temperatures than solutions prepared from either of these solvent components alone. These advantages prevail at any temperature. Accordingly, a solution containing a given concentration of active ingredient will remain liquid at a lower temperature than a solution containing the same concentration of active ingredient but prepared in toluene alone or in methanol alone. This is illustrated in the accompanying drawing which will be discussed in detail with reference to the appended examples.

As above set forth, the concentration of active ingredient in the solution will depend upon the temperature of the geographical areas in which the metal deactivator solution is to be used. For example, in areas of extremely low temperatures, the concentration of active ingredient will be within the range of from about 30% to about 50% by weight of the solution. In intermediate temperature areas, the concentration of active ingredient may range from 40% to 60%. In areas of moderate temperatures or, in cases where the solution is kept indoors or heated prior to use, the solution may contain from about 60% to about 80% by weight of active ingredient. Thus, it will be seen that the advantages of the novel composition of the present invention prevail at a wide range of temperatures and that the percent of active ingredient in the solution will vary accordingly. However, at any given temperature, the novel solution of the present invention offers advantages over the use of either of these solvent components alone. Thus, any general teachings in the prior art that aromatic hydrocarbons or alcohols may be used obviously do not teach the important concept and will not result in the improved deactivator solutions of the present invention.

The metal deactivator functions in a manner entirely distinct from that of a gum inhibitor which normally is incorporated in gasoline. The gum 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 gum formation per se to any considerable extent, but serves primarily to deactivate the metal constituents and thereby to destroy the catalytic effect thereof to enhance oxidative reactions.

Any suitable gum inhibitor may be employed along with the metal deactivator composition of the present invention. These gum inhibitors are well known and generally include various phenols, amines, aminophenols, as well as fractions of wood tar, oil, etc. A particularly suitable gum inhibitor comprises N,N'-di-secondary-butyl-p-phenylene diamine. Another particularly suitable gum inhibitor comprises a mixture of a major proportion of N-butyl-p-aminophenol and a minor proportion of N,N'-di-butyl-p-phenylene diamine. It is understood that the gum inhibitor may be prepared as a mixed product with the metal deactivator, and the mixed solution marketed as a single commodity.

The gum inhibitor usually is incorporated in gasoline in a concentration of from about 0.0005% to about 1% by weight, and the metal deactivator generally is incorporated in the gasoline in a smaller concentration, which may range from about 0.0001% to about 0.5% by weight (based on active constituent). When used in other substrates, it is understood that lower or higher concentrations may be used which generally will be below about 1% by weight of the substrate.

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 active metal deactivator constituent is disalicylalpropylenediamine and was prepared by the condensation of 2 mols of salicylaldehyde with 1 mol of propylenediamine (1,2-diaminopropane). It was prepared as a solution in the solvents set forth below, the active constituent comprising 50% by weight of the total composition.

The solvent mixture used in this example is toluene and methanol. The following table reports the solubility of disalicylalpropylenediamine in various mixtures of these solvents at 36° F.

Table I

Solvent		Solubility of disalicylalpropylenediamine, g./100 g. of solvent
Percent Toluene	Percent Methanol	
100	0	120
95	5	156
91	9	200
88	12	208
76	24	236
56	44	44
0	100	6

From the data in the above table, it will be noted that the use of methanol in concentrations above about 25% resulted in lower solubility of disalicylalpropylenediamine. On the other hand, it will be noted that use of the mixed methanol-toluene solvent, the former in a concentration of from about 5% to about 25% by weight of the solvent, resulted in a considerable increase in the solubility of disalicylalpropylenediamine.

EXAMPLE II

Another series of solubility runs made using the disalicylalpropylenediamine and toluene-methanol solvent

described in Example I. This series of runs was made at 5° F., and the results thereof are reported in the following table:

Table II

Solvent		Solubility of disalicylalpropylenediamine, g./100 g. of solvent
Percent Toluene	Percent Methanol	
100	0	42
95	5	53
91	9	71
88	12	69.5
84	16	59.5
74	26	50
69	31	49.5
58	42	34.5
52	48	29

Here again, it will be noted that the same general results are obtained at 5° F. as compared to the runs made at 36° F. as reported in Example I. Also, it will be noted that the solubility of disalicylalpropylenediamine, even in the mixed solvent, is considerably lower than at 36° F. However, the solubility at this low temperature is the most important for the following reasons: (1) The freezing difficulties are encountered at the low temperature and, in order to be satisfactorily used, the metal deactivator composition must remain fluid at the low temperature. (2) A solution which is fluid at the low temperature will be fluid at a higher temperature and therefore will not present any freezing problems at the higher temperature.

EXAMPLE III

Another series of solubility runs was made using the disalicylalpropylenediamine described in Example I and toluene-methanol solvent. This series of runs was made at 70° F. and the results thereof are reported in the following table:

Table III

Solvent		Solubility of disalicylalpropylenediamine, g./100 g. of solvent
Percent Toluene	Percent Methanol	
100	0	350
94.8	5.2	460
90.1	9.9	525
76.5	23.5	520
0	100	190

Here again, it will be noted that the same general results are obtained at 70° F. as were obtained at 36° F. and at 5° F. as reported in Examples I and II. Thus, as hereinbefore set forth, the advantages of the mixed solvent of the present invention apply regardless of the particular temperature at which the metal deactivator solution is to be used.

In order to illustrate the criticality of the components of the solvent mixture, the data of Tables I, II and III have been plotted in the accompanying drawing on semi-log paper. Referring to the drawing, it will be noted that the solvent mixtures in which the methanol comprises from about 5% to about 25% by weight and the toluene comprises from about 75% to about 95% by weight results in considerably higher solubility of disalicylalpropylenediamine. Another advantage to the present invention is a reduction in shipping costs because of the lower amount of solvent included in the composition. However, as hereinbefore set forth, in other instances it is desired to prepare solutions containing a lower concentration of active ingredient. The particular proportions of active ingredient and solvent therefore will vary, depending upon the ambient conditions at which the metal deactivator solution will be used. However, regardless of the specific concentration of active ingredient in the mixed solvent, the solution will remain liquid at a lower temperature than otherwise obtainable when using either of the solvent components alone.

EXAMPLE IV

The metal deactivator of this example comprised 50% by weight of active ingredient, 45% by weight of toluene and 5% by weight of methanol. The acitve ingredient contains 95% by weight of the condensation product of 2 mols salicylaldehyde with 1 mole of propylenediamine (1,2-diaminopropane). This solution remains stable at temperatures above 5° F.

EXAMPLE V

The metal deactivator of this example comprised 41.5% by weight of active ingredient, the active ingredient being the same as the one described in Example IV. The solvent consisted of 58.5% by weight of the total solution and comprised 9% by weight of methanol and 91% by weight of toluene.

EXAMPLE VI

The active metal deactivator component of this example was prepared by the condensation of 2 mols of salicylaldehyde with 1 mol of propylenediamine (1,2-diaminopropane). A solution comprising 60% by weight of the active metal deactivator, 36% by weight of toluene and 4% by weight of methanol is prepared.

The above solution is utilized in the stabilization of a thermally cracked gasoline. The unstabilized gasoline has an Induction Period of 55 minutes. Upon the addition of 0.1% by weight of an antioxidant comprising N,N'-di-secondary-butyl-p-phenylene diamine, the Induction Period of the gasoline is increased to 1050 minutes. However, upon the addition of 1 part per million (1 mg. per liter) of copper, in the form of copper oleate, the Induction Period of the gasoline drops to 55 minutes. Upon the addition of 7 parts per million of the copper deactivator solution described above, the Induction Period of the gasoline is raised to 995 minutes. It will be noted that the metal deactivator solution of the present invention serves to offset the deleterious effect of the copper and produces a final gasoline of high stability.

EXAMPLE VII

The metal deactivator of this example comprised disalicylal-1,3-diaminobutane and was prepared by the condensation of 2 mols of sailicylaldehyde with 1 mol of 3,3-diaminobutane. A composition of 44% by weight of disalicylal-1,3-diaminobutane in toluene has a melting point of about 178° F. However, the melting point is considerably decreased by utilizing a mixed solvent comprising 90% toluene and 10% methanol.

EXAMPLE VIII

A metal deactivator composition is prepared by dissolving the mixed condensation product of 2 ortho-hydroxy aromatic aldehydes with an alkylene polyamine in a mixed solvent comprising 90% by weight of xylene and 10% by weight of isopropyl alcohol.

EXAMPLE IX

The metal deactivator composition of this example comprises 40% by weight of salicylaldehydepropylenediamine in a mixed solvent comprising 85% by weight of benzene and 15% by weight of secondary butyl alcohol.

EXAMPLE X

The metal deactivator solution described in Example VI is used for the stabilization of lard. The lard has a normal stability period of four hours as determined by the Active Oxygen Method. This method is a standard test for determining the stability of lard. In general, this

test comprises bubbling air through a sample of the lard and periodically determining the peroxide number. The results are reported as the number of hours required to reach a peroxide number of 20.

In order to determine the effect of metal, a 3" strip of 18 gauge copper wire is added to a sample of the lard. The stability of the lard is reduced from four hours to one hour in the presence of the copper. However, upon the addition of the metal deactivator solution described above, the stability of the lard is increased to four hours. Here again, it will be noted that the metal deactivator solution of the present invention serves to effectively offset the deleterious effect of the copper.

We claim as our invention:

1. A solution of from about 30% to about 80% by weight of disalicylalpropylenediamine in from about 20% to about 70% by weight of a solvent mixture of from about 5% to about 25% by weight of methanol and from about 75% to about 95% by weight of toluene.

2. A solution of from about 40% to about 60% by weight of disalicylalpropylenediamine in from about 40% to about 60% by weight of a solvent mixture of from about 5% to about 25% by weight of methanol and from about 75% to about 95% by weight of toluene.

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