Patented Dec. 12, 1950 2,533,205

UNITED STATES PATENT OFFICE

2,533,205

METAL DEACTIVATORS

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No Drawing. Application October 27, 1947, Serial No. 782,463

4 Claims. (Cl. 44—73)

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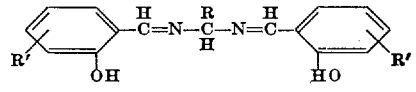
The present invention relates to a method of stabilizing organic compounds, and particularly to the stabilization of organic substances against deterioration by oxygen catalyzed in the presence of or by contact with certain oxidation promoters. While the present invention is applicable to preventing such deterioration of edible fats and oils, foods, monomers, 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 process the gasoline is contacted with a copper-containing reagent. 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 occurring 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 stability of the gasoline.

In one embodiment the present invention relates to a method of stabilizing an organic substance subject to oxidative deterioration, which comprises adding thereto a metal deactivator prepared by condensing 2 mols of ammonia with at least 2 mols of an ortho-hydroxy aromatic aldehyde.

In a specific embodiment the present invention relates to a method of stabilizing cracked gasoline containing copper, which comprises adding thereto hydrosalicylamide in an amount sufficient to suppress the catalytic effect of said copper.

The novel metal deactivator of the present invention may be represented by the following general formula:



where R is selected from the group consisting of hydrocarbon, hydroxy hydrocarbon, alkoxy hydrocarbon and alkoxyhydroxy hydrocarbon radicals, and R' is selected from the group consisting of hydrogen, alkyl and alkoxy radicals.

It is readily apparent that the present invention contemplates an extensive number of compounds which may be prepared and used within the broad scope of the present invention. It is

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understood that, while all of these compounds will have some potency as metal deactivators, they are not necessarily equivalent and that the choice as to the particular metal deactivator to be used in any given instance will depend upon the particular organic material to be treated.

Typical examples of the metal deactivators of the present invention are illustrated by the following specific compounds.

Where R in the above formula is a hydrocarbon group, it may comprise an aryl, alkaryl, alkyl, aralkyl or cycloalkyl group. Where R is an aryl group, the metal deactivator will comprise phenyl-bis-(salicylalamino)-methane, naphthyl-bis-(salicylalamino)-methane, etc. Where R comprises an alkyaryl group, the metal deactivator will comprise such compounds as a methyl-phenyl - bis - (salicylalamino) - methane, ethyl-phenyl - bis - (salicylalamino - methane, propyl-phenyl - bis - (salicylalamino) - methane, butyl-phenyl - bis - (salicylalamino) - methane, amyl-phenyl-bis-(salicylalamino)-methane, etc. It is understood that the alkyl group may be in either the ortho, metal or para position, and also that the aryl group may contain 2 or more alkyl radicals attached thereto.

Where R comprises an alkyl radical the metal deactivator will include such compounds as 1,1-bis-(salicylalamino)-ethane, 1,1-bis-(salicylalamino)-propane, 1,1-bis-(salicylalamino)-butane, 1,1-bis-(salicylalamino)-pentane, 1,1-bis-(salicylalamino) - hexane, 1,1 - bis - (salicylalamino) - heptane, 1,1 - bis - (salicylalamino)-octane, etc. Where R comprises an aralkyl group, the metal deactivator will include such compounds as 1,1 - bis - (salicylalamino) - 2 - phenyl ethane, 1,1-bis-(salicylalamino)-3-phenyl propane, 1,1-bis-(salicylalamino)-4-phenyl butane, etc.

Where R in the above formula comprises a cycloalkyl group, the metal deactivator will be cyclohexyl-bis-(salicylalamino)-methane which may or may not contain alkyl, hydroxy and/or alkoxy groups attached to the cyclohexyl ring.

It will be noted that the above compounds comprise the class in which R' of the above general formula is hydrogen. Compounds in which R in the above formula comprises a hydroxy hydrocarbon are preferred metal deactivators. This class of metal deactivators are represented by hydrosalicylamide which may otherwise be named (2 - hydroxyphenyl) - bis - (salicylalamino)-methane. Preferred metal deactivators also include compounds in which the R radical comprises a alkoxyhydroxy or alkylhydroxy aryl

group, the latter being included within the broad class of hydroxy hydrocarbon substituents. Preferred metal deactivators of the alkoxyhydroxy hydrocarbon class include (2-hydroxy-3-methoxyphenyl)-bis-(2 - hydroxy-3-methoxybenzalamino)-methane, (2-hydroxy-3-ethoxy-phenyl)-bis - (2 - hydroxy - 3 - ethoxybenzalamino)-methane, (2-hydroxy-3-propoxyphenyl)-bis-(2-hydroxy - 3 - propoxybenzalamino) - methane, etc. It will be noted that the three phenyl rings all contain similar substituent groups in the same positions. This is generally preferred because of ease of manufacture as will be hereinafter described in further detail. It will also be noted that in these compounds, the R' groups represent alkoxy radicals.

Where R in the above general formula comprises an alkylhydroxy radical, the metal deactivator will include such compounds as (2-hydroxy-5 - methylphenyl) - bis - (2 - hydroxy - 5 - methyl-benzalamino)-methane, (2-hydroxy-5-ethylphenyl) - bis - (2 - hydroxy - 5 - ethyl - benzalamino)-methane, (2-hydroxy-5-propylphenyl)-bis - (2 - hydroxy - 5 - propyl - benzalamino)-methane, (2-hydroxy-5-tert-butyl-phenyl)-bis-(2-hydroxy-5-tert-butyl-benzalamino)-methane, (2 - hydroxy - 5 - amyl - phenyl) - bis - (2 - hydroxy-5-amyl-benzalamino)-methane, etc. It is understood that the akyl radicals may be attached to different positions on the aryl rings and also that two or more alkyl groups may be attached to the aryl rings. It will be noted that these metal deactivators comprise compounds in which the R' groups are alkyl radicals.

Where R in the above general formula comprises an alkoxy hydrocarbon group, the metal deactivators will include such compounds as (2 - methoxyphenyl) - bis - (salicylalamino)-methane, (2 - ethoxyphenyl) - bis - (salicylalamino)-methane, (2-propoxyphenyl)-bis-(salicylalamino)-methane, etc. It is understood that these compounds may contain alkyl groups attached to the ring in addition to the alkoxy groups. It will be noted that these metal deactivators comprise compounds in which the R' groups in the above general formula are hydrogen radicals.

Metal deactivators of the present invention are readily prepared by the condensation of 2 mols of ammonia with 3 mols of aldehydes of which at least 2 mols are an ortho-hydroxy aromatic aldehyde. As hereinbefore set forth, preferred metal deactivators comprise those in which the R group is a substituted phenyl group having the same substituents as the aromatic aldehyde originally used to prepare the metal deactivator. This simplifies preparation of the metal deactivator, which then is readily prepared by the condensation of 2 mols of ammonia with 3 mols of the desired ortho-hydroxy aromatic aldehyde. Thus, hydrosalicylamide is readily prepared by adding concentrated ammonium hydroxide to an alcoholic solution of salicylaldehyde and, after the reaction has gone to completion, the water formed in the reaction is removed and the final product is recovered in any suitable manner. Other metal deactivators in which the 3 phenyl rings contain hydroxy and alkyl or alkoxy radicals are similarly prepared by the condensation of 2 mols of ammonia with 3 mols of the desired substituted aromatic aldehyde. Thus, for example, 3 mols of ortho-vanillin may be condensed with 2 mols of ammonia. When the R group is different than the other phenyl rings, the desired reactants are mixed in the proper proportions to

form the desired metal deactivator as, for example, the condensation of 2 mols of ammonia with 2 mols of salicylaldehyde and 1 mol of ortho-vanillin.

In general, it is preferred that the total number of carbon atoms in the metal deactivator be not greater than about 30, as it has been found that, within certain limits, the potency of the deactivator decreases with inclusion of hydrocarbon radicals of high molecular weight.

The metal deactivators of the present invention are generally utilized in addition to gum inhibitors. The function of the metal deactivator is entirely distinct from the function of the gum inhibitor. For example, 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 only to deactivate the metal compounds and thereby destroy the catalytic effect thereof to enhance oxidative reactions.

Any suitable gum inhibitor may be employed along with the metal deactivator of the present invention. These gum inhibitors are well known and generally include various phenols, amines, amino phenols, as well as fractions of wood tar oil, etc. Some of these inhibitors are marketed in the form of a solution in a suitable solvent such as alcohol, ether, 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-n-butyl-p-aminophenol and a minor proportion of N-N'-di-n-butyl-p-phenylene diamine in an alcoholic solvent.

The gum inhibitors are usually added to gasoline in concentrations of from about 0.001% to about 0.1% by weight and the metal deactivator is generally added to gasoline in a smaller concentration which may range from about 0.0005% to about 0.05% by weight. The metal deactivator may be marketed as such or dissolved in a suitable solvent which is not reactive therewith. In some cases, when a solvent is used for the gum inhibitor, the same solvent may be used for the metal deactivator and thus the gum inhibitor and metal deactivator, when desired, may be prepared as a mixture in a suitable solvent and the combined inhibitor and deactivator marketed as a single commodity of a two-fold purpose.

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

The metal deactivators of the present invention were prepared by the condensation of the reactants as shown in the following table. These metal deactivators were tested in a Pennsylvania cracked gasoline, and the results are reported as the induction period in minutes. The induction period is determined by the oxygen bomb stability test which is the standard method of evaluating the storage stability of gasoline.

The Pennsylvania cracked gasoline used in these tests had an induction period of 90 minutes. Upon the addition of 0.005% by weight of a gum inhibitor comprising N-N'-di-secondary butyl-p-phenylene diamine, the induction period was increased to 470 minutes. To show the deleterious effect of metal, copper in the form of copper oleate was added in an amount of 1 milligram of copper per liter of gasoline to different samples of the gasoline containing gum inhibitor.

Upon the addition of the copper, the induction period of the inhibited gasoline fell to 180 minutes. 0.01% by weight of the metal deactivator was added to different samples of the inhibited gasoline containing copper, and the induction period was increased as shown in the following table:

Table

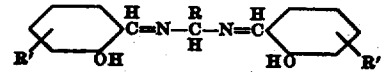
Compound	Reactants	M. P.	Induction Period
		° C.	*Minutes*
hydrosalicylamide....	salicylaldehyde, ammonia.	165–6	485
(2-hydroxy-3-methoxyphenyl)-bis-(2-hydroxy-3-methoxybenzalamino)-methane.	2-hydroxy-3-methoxybenzaldehyde, ammonia.	148–149	480
(2-hydroxy-5-tertbutylphenyl)-bis-(2-hydroxy-5-tertbutylbenzalamino)-methane.	2-hydroxy-5-tertbutylbenzaldehyde, ammonia.	85–87	480
(2-hydroxy-5-methylphenyl)-bis-(2-hydroxy-5-methylbenzalamino)-methane.	2-hydroxy-5-methylbenzaldehyde, ammonia.	74–76	470
1,1-bis-(salicylalamino)-butane.	n-butyraldehyde (1 mol), salicylaldehyde, (2 mols), ammonia.	77–79	310
1,1-bis-(salicylalamino)-heptane.	heptaldehyde (1 mol), salicylaldehyde (2 mols), ammonia.	77–78	350
phenyl-bis-(salicylalamino)-methane.	benzaldehyde (1 mol), salicylaldehyde (2 mols), ammonia.	115–117	[1] 265

[1] Metal deactivator added in an amount of 0.001% by weight.

It will be noted that the metal deactivators of the present invention increased the induction period of the gasoline. The preferred metal deactivators actually increased the induction period to its original inhibited value and thereby served to offset the deleterious effect of the added metal.

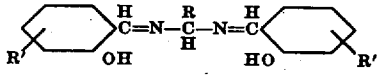
I claim as my invention:

1. An organic substance containing a metal compound which normally catalyzes oxidative deterioration and additionally containing a small amount of a metal deactivator having the general formula



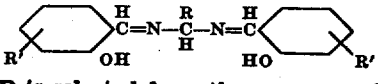
where R is selected from the group consisting of hydrocarbon, hydroxy hydrocarbon, alkoxy hydrocarbon and alkoxyhydroxy hydrocarbon radicals, and R′ is selected from the group consisting of hydrogen, alkyl and alkoxy radicals.

2. Gasoline containing unsaturated hydrocarbons which tend to form gums and a metal compound which normally catalyzes oxidative deterioration and additionally containing a small amount of a metal deactivator having the general formula



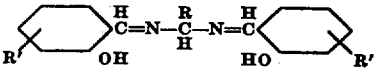
where R is selected from the group consisting of hydrocarbon, hydroxy hydrocarbon, alkoxy hydrocarbon and alkoxyhydroxy hydrocarbon radicals, and R′ is selected from the group consisting of hydrogen, alkyl and alkoxy radicals.

3. Cracked gasoline containing a small amount of a gum inhibitor to prevent gum formation and a smaller amount of a metal deactivator having the general formula



where R is selected from the group consisting of hydrocarbon, hydroxy hydrocarbon, alkoxy hydrocarbon and alkoxyhydroxy hydrocarbon radicals, and R′ is selected from the group consisting of hydrogen, alkyl and alkoxy radicals.

4. A metal deactivator having the general formula



where R is selected from the group consisting of hydrocarbon, hydroxy hydrocarbon, alkoxy hydrocarbon and alkoxyhydroxy hydrocarbon radicals, and R′ is selected from the group consisting of hydrogen, alkyl and alkoxy radicals.

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