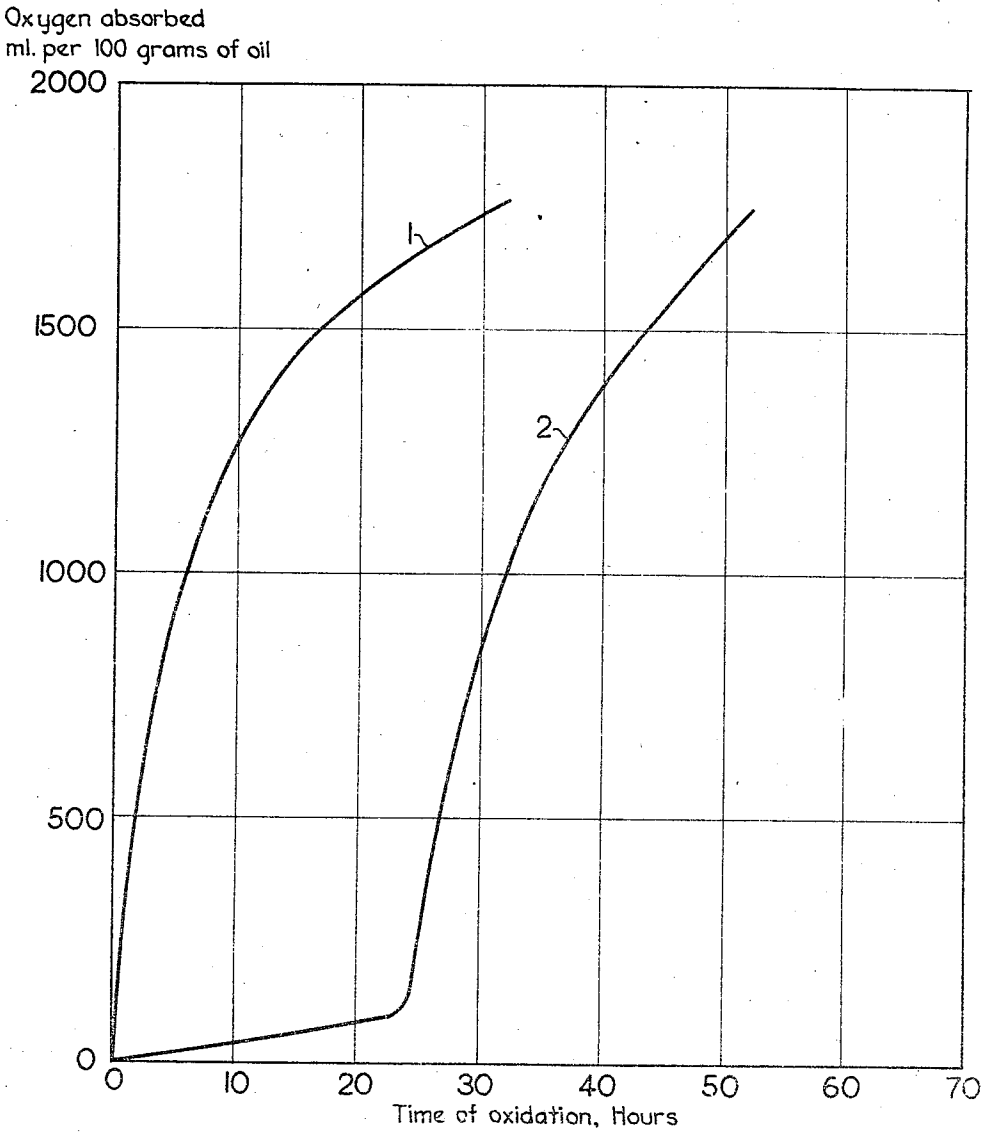
June 9, 1942. E. R. WHITE ET AL 2,285,878

COMPOSITION CONTAINING METAL DEACTIVATORS AND THE METHOD OF PREPARING THE SAME

Filed June 10, 1940



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By their Attorney: [signature]

Patented June 9, 1942

2,285,878

UNITED STATES PATENT OFFICE

2,285,878

COMPOSITION CONTAINING METAL DEACTIVATORS AND THE METHOD OF PREPARING THE SAME

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Application June 10, 1940, Serial No. 339,790

11 Claims. (Cl. 252—51)

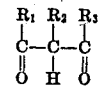
This invention relates to a method for the stabilization of organic substances and particularly to the protection of organic substances against deterioration by oxidation which is catalyzed by the presence of or by contact with certain oxidation promoters. An important application of this invention resides in the reduction of the amount of gum formed in gasoline during storage due to the presence of small amounts of certain metals, their compounds or both. Another application is as a stabilizer for lubricating oils to retard discoloration and sludge formation, etc., due to catalytic oxidation.

It is the purpose of this invention to provide a class of deactivator compounds which reduce the catalytic effect of metal oxidation promoters, more particularly of copper, iron, chromium, lead and the compounds of copper, chromium and lead. It is another purpose to provide deactivators which when added to organic substances will remain active for a considerable length of time when subjected to oxidizing influences. Still another purpose is to render hydrocarbon oils insensitive to the catalytic oxidation of metals such as iron and copper for invariably, during their useful life, the oils come in contact with one or the other of these metals.

Organic substances normally contact metals, or frequently contain small amounts of metals usually dissolved in the form of a soluble salt, and it has been observed that the presence of such metals frequently has a detrimental effect on the stability of the substances. Inasmuch as bare traces of the metals may be very harmful and since removal of these last traces is extremely difficult, it is often not possible to eliminate this troublesome catalyst of the oxidation reaction.

It has already been suggested to reduce the susceptibility of organic substances to oxidation induced by the presence of copper, by adding to the organic substance certain deactivators which have the property of rendering the copper inactive. The deactivators heretofore suggested, comprise products of condensation of one mol of an aliphatic or aromatic primary diamine with two mols of salicylaldehyde or similar compounds. It is known for example, that the addition of these deactivators reduces the gum formation in the presence of dissolved copper as determined by the A. S. T. M. air jet method and also increases the induction period as tested by the Voorhees and Eisinger method described in S. A. E. J. 24,584 (1929).

It has been discovered that products obtained by reacting compounds of the general formula



with certain primary amines, under conditions to eliminate water by the interaction of one of the carbonyl and primary amine radicals, possess the property of deactivating metallic iron, copper, chromium, lead and the compounds of copper, chromium and lead. Many of these products retain their activity after exposure to oxidizing influences.

The action of our deactivators appears to be specific for certain metals and their compounds. Different types of organic substances may be protected from the catalytic effect of metal oxidation promoters. The deactivators must be at least slightly soluble in the organic substance by itself or in a mutual solvent. Neutral and basic substances are in general more susceptible to the action of the deactivators than acids.

The general formula above covers diacyl compounds, or more specifically beta diketones wherein R_1, R_2, and R_3 represent radicals selected from the group consisting of hydrogen, alkyl, aryl or aralkyl radicals, preferably containing a total of not more than 20 carbon atoms.

Suitable diacyl compounds are, for example, acetyl acetone, propionyl acetone, acetyl butyryl methane, acetyl isobutyryl methane, acetyl caproyl methane, 2 methyl 1.3 propane-dione, 2 ethyl 3.5 heptane-dione, acetyl aceto phenone, propionyl aceto phenone, butyryl aceto phenone, isobutyryl aceto phenone, phenyl acetyl acetone, phenyl propionyl acetone, etc.

Amines capable of forming deactivators with the above diacyl compounds comprise certain aliphatic and carbocyclic di- and higher poly-amines.

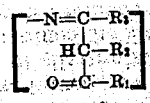
The aliphatic poly-amines may be any aliphatic amine containing from 2 to 12 carbon atoms, which may be arranged in a continuous or discontinuous chain, and contain at least two primary amino groups directly attached to different carbon atoms. The carbon chain may contain oxygen, sulfur or nitrogen and the amino groups may be attached to carbon atoms which are interconnected by oxygen, sulfur or nitrogen linkages.

Suitable aliphatic amines are, for example, ethylene diamine, 1.2 propylene diamine, 1.3 propylene diamine, 1.10 decylene diamine, tetra methyl 1.2 diamino ethane, diethyl dimethyl 1.2

diamino ethane, 1.4 diamine diisobutyl, 1.6 diamino diisoamyl, diamino isopropanol, diamino butanols, diamino pentanols, diamino diethyl ether, amino ethyl amino propyl ether, corresponding thio or imino ethers, etc.

Suitable aryl-aliphatic amines are those in which one primary amino group is connected to an aromatic nucleus through a linkage comprising at least one carbon atom. Additional primary amino radicals may be attached to different carbon atoms of the same linkage or forming different linkages with the aromatic nucleus. Carbon linkages may consist of continuous or discontinuous carbon chains which may contain oxygen, sulfur or nitrogen. Suitable carbocyclic amines are for instance, diamino diethyl-benzene, amino ethyl amino propyl benzene, phenyl diamino ethane, phenyl amino ethyl amino ethyl ether, phenyl amino ethyl amino ethyl thioether, phenyl amino ethyl amino propyl ether, etc.

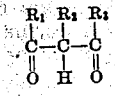
The reaction compounds of this invention are products formed by the reaction of one mol of a poly-amino compound with at least two mols of a diacyl compound. Thus all compounds of this invention contain at least two radicals as follows:



Reaction products may be represented by the general formula

$$(Y{=}N)_n{-}Z$$

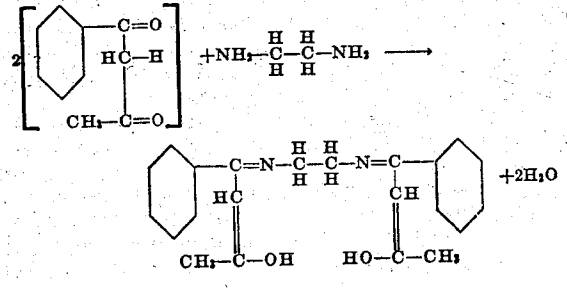
wherein Y represents a radical derived by elimination of an oxygen atom from a beta dicarbonyl compound of the general formula



wherein R_1, R_2 and R_3 represent radicals selected from the group consisting of hydrogen, alkyl, aryl or aralkyl radicals containing not more than a total of 20 carbon atoms; Z represents an aliphatic or an aryl-aliphatic radical of not more than 12 carbon atoms which may contain hydroxy or primary amino radicals and ether, thioether and imino ether linkages and n is 2 or more.

In analogy to the above compounds wherein n is 2, we may also use mixed compounds which contain one dicarbonyl radical as shown above while another dicarbonyl radical is replaced by a salicylal radical of the type described in the copending application Serial No. 339,508, filed June 8, 1940. Such mixed compounds may, for example, be obtained by reacting a mixture of beta diketone and salicylaldehyde with one of the polyamines described earlier.

A typical deactivator is the product prepared by reacting 2 mols of acetyl aceto phenone with one mol of ethylene diamine and yielding dibenzoyl acetonyl ethylene diamine:



It is desirable that the compounds of this invention have molecular weights which are not excessively high because the reaction between the deactivator compounds and the metal is apparently one in which one molecule of a symmetric deactivator is capable of capturing and deactivating not more than one atom of a metal. It is therefore desirable to keep the amount of dead load in the molecule of the deactivators to a minimum.

Some deactivators are active primarily before oxidation while others are effective both before and after oxidation.

The effectiveness of various compounds as metal deactivators and suppressors of oxidation catalyzed by metals may be estimated by measuring their activities under at least two conditions, namely before and after oxidation. Thus, for example, as applied to a gasoline, one may measure first, the extent to which these compounds overcome the adverse effect of the metal in lowering the induction period; second, the extent to which they reduce the initial copper dish gum value of the gasoline; and third, the extent to which they maintain low copper dish gum after accelerated oxidation.

To illustrate how the metal deactivators of this invention suppress the catalytic activity, for example of copper, the deactivators were tested in gasoline containing 1 part per million of dissolved copper in the form of copper phenyl propionate. The results of tests are shown in Table I:

Table I

Deactivator added 2.5 mg./100 ml. gasoline	Induction period, hours		Copper dish gum	
	No copper	1 P.P.M. dissolved copper	Initial	After 1 hour accelerated oxidation
None	4.58	1.67	59, 66	128, 133
Dibenzoyl acetonyl ethylene diamine	4.67	3.83	11, 16	19, 20
Diacetyl acetonyl ethylene diamine	6.50	5.83	12, 17	8, 10
None	6.17	2.33	38, 39	54, 55

The effect of the deactivators in contact with lubricating oil is illustrated by the attached drawing representing a graph wherein is plotted the length of time in hours of oxidation against the amount of oxygen absorbed in the presence of metallic iron.

In this test, the oil is exposed to pure oxygen at atmospheric pressure and at a temperature of 150° C.

On the ordinate of the graph is plotted the mols of oxygen absorbed, on the abscissa is indicated the time of oxidation. Two curves are shown, curve 1 representing the art of oxygen absorption in the absence of any deactivator and curve 2 representing the rate of oxygen absorption under identical conditions in the presence of 0.1% by weight of diacetyl acetonyl ethylene diamine.

It will be seen that the metallic iron was deactivated for a considerable length of time under the extremely severe conditions of the test.

Our deactivators also suppress the catalytic oxidation which may be caused by a combination of the various metal oxidation promoters. Thus, for example, if gasoline containing dissolved copper is stored in an iron drum, our compounds deactivate both the dissolved copper and metallic iron.

Our products are active in various organic substances which are subject to deterioration by oxidation and which substances during their useful life come in contact with any of the metals or their compounds hereinbefore enumerated. Thus, various refined and semi-refined hydrocarbon oils may be stabilized, such as gasoline, kerosene, special boiling point solvents, Diesel fuels, spray oils, lubricating oils, etc., pure hydrocarbons such as benzene, toluene, various liquid olefins, etc. Other substances capable of being protected are, for example, animal fats and oils, vegetable fats and oils, soaps, photographic developers, both natural and synthetic sulfonated and sulfated oils, essential oils, perfumes, cellulose acetate, rubber, various resins, etc.

The presence of antioxidants and other compounds in the substance to be desensitized, which compounds have the property of modifying the susceptibility of these substances toward noncatalytic oxidation such as ordinary oxidation inhibitors as used in gasoline, lubricating oil, rubber, fats, soaps, etc., may have an influence on the activity of deactivators, promoting or retarding their effectiveness.

The deactivators of this invention may be used in conjunction with other addition agents, for example, in gasoline, together with anti-knock compounds and anti-oxidants, blooming agents, anti-corrosives, extreme pressure compounds, detergents, etc., or in Diesel fuels together with knock suppressors, anti-oxidants, etc. It is, however, desirable that the addition agent shall not raise the acidity of the substance to be desensitized to the point of greatly diminishing the activity of the deactivators.

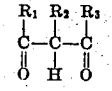
The amounts of our deactivators to be added to the substances effectively to suppress the catalytic action of the metals or their compounds will naturally vary with the stability requirements of the treated product, as well as with the amount of metal contained in the organic substance if dissolved metal is the source of the instability. In general, quantities ranging from about .01% to 1% are useful and provide the necessary protection, although under certain circumstances, amounts outside of these limits may be used.

The metal deactivators may be added to the organic substance to be stabilized in any desired form. They may be added in solid or liquid form, mixed with other addition agents or dissolved in a solvent.

Some organic substances dissolve metals during their use. This, for instance, is the case with lubricating oils, electrical oils, gasolines, etc. When treating such substances with our compounds, it is often desirable to use an amount considerably in excess of that which is required to give it adequate initial protection. In such cases, the proper amounts of the deactivator may if desired be added during the use of the organic substance as may be required from time to time.

We claim as our invention:

1. An organic substance subject to deterioration thru oxidation, which substance during its useful life comes in contact with an oxidation promoter selected from the group consisting of metallic iron, copper, chromium, lead and compounds of copper, chromium and lead, containing a small amount of a reaction product of an aliphatic poly primary amine having 2 to 12 carbon atoms with two mols of a beta dicarbonyl compound formed by the elimination of water by interacting not more than one of the carbonyl radicals of each molecule of the dicarbonyl compound with a primary amino radical, said beta dicarbonyl compounds having the general formula



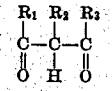
wherein R_1, R_2 and R_3 represent radicals selected from the group consisting of hydrogen, alkyl, aryl and aralkyl radicals containing a total of not more than 20 carbon atoms said reaction product being at least slightly soluble in said organic substance and said organic substance being susceptible to the inhibiting action of said reaction product.

2. The substance of claim 1 which contains .01% to 1% by weight of the reaction product.

3. An organic substance subject to deterioration thru oxidation, which substance during its useful life comes in contact with an oxidation promoter selected from the group consisting of metallic iron, copper, chromium, lead and compounds of copper, chromium and lead, containing a small amount of a deactivator having the general formula

$$(Y{=}N)_n{-}Z$$

wherein Y represents a radical derived by elimination of an oxygen atom from a beta dicarbonyl compound of the general formula

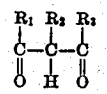


wherein R_1, R_2 and R_3 represent radicals selected from the group consisting of hydrogen, alkyl, aryl and aralkyl radicals containing no more than a total of 20 carbon atoms, Z represents an aliphatic radical of not more than 12 carbon atoms and n is integer of 2 or more said deactivator being at least slightly soluble in said organic substance and said organic substance being susceptible to the action of said deactivator.

4. An organic substance subject to deterioration thru oxidation, which substance during its useful life comes in contact with an oxidation promoter selected from the group consisting of metallic iron, copper, chromium, lead and compounds of copper, chromium and lead, containing a small amount of a deactivator having the general formula

$$(Y{=}N)_n{-}Z$$

wherein Z represents an aliphatic radical having 2 to 12 carbon atoms and containing a linkage of an element selected from the group consisting of oxygen, nitrogen and sulfur, Y represents a radical derived by elimination of an oxygen atom from a beta dicarbonyl compound of the general formula

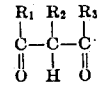


wherein R_1, R_2 and R_3 represent radicals selected from the group consisting of hydrogen, alkyl, aryl and aralkyl radicals containing a total of not more than 20 carbon atoms and n is either 2 or more said deactivator being at least slightly soluble in said organic substance and said organic substance being susceptible to the action of said deactivator.

5. An organic substance subject to deterioration thru oxidation, which substance during its useful life comes in contact with an oxidation promoter selected from the group consisting of metallic iron, copper, chromium, lead and compounds of copper, chromium and lead, is capable of dissolving diacetyl acetonyl ethylene diamine and is susceptible to its deactivating action containing a small amount of diacetyl acetonyl ethylene diamine.

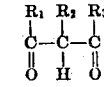
6. An organic substance subject to deterioration thru oxidation, which substance during its useful life comes in contact with an oxidation promoter selected from the group consisting of metallic iron, copper, chromium, lead and compounds of copper, chromium and lead, is capable of dissolving dibenzoyl acetonyl ethylene diamine and is susceptible to its deactivating action containing a small amount of dibenzoyl acetonyl ethylene diamine.

7. A gasoline of reduced copper dish gum containing a small amount of a reaction product of an aliphatic poly primary amine having 2 to 12 carbon atoms with two mols of a beta dicarbonyl compound formed by the elimination of water by interacting not more than one of the carbonyl radicals of each molecule of the dicarbonyl compound with a primary amino radical, and said beta dicarbonyl compounds having the general formula



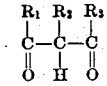
wherein R_1, R_2 and R_3 represent radicals selected from the group consisting of hydrogen, alkyl, aryl and aralkyl radicals containing a total of not more than 20 carbon atoms said reaction product being at least slightly soluble in said gasoline.

8. A lubricating oil of improved oxidation stability in contact with iron comprising a mineral lubricating oil containing a small amount of a reaction product of an aliphatic poly primary amine having 2 to 12 carbon atoms with two mols of a beta dicarbonyl compound formed by the elimination of water by interacting not more than one of the carbonyl radicals of each molecule of the dicarbonyl compound with a primary amino radical, said beta dicarbonyl compounds having the general formula



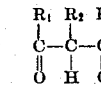
wherein R_1, R_2 and R_3 represent radicals selected from the group consisting of hydrogen, alkyl, aryl and aralkyl radicals containing a total of not more than 20 carbon atoms said reaction product being at least slightly soluble in said lubricating oil.

9. The method of increasing the stability of organic compounds subject to deterioration thru oxidation in contact with oxidation promoters selected from the group consisting of metallic iron, copper, chromium, lead and compounds of copper, chromium and lead, comprising incorporating in said organic compounds a small amount of a reaction product of a primary amine having 2 to 12 carbon atoms and a beta dicarbonyl compound, formed by the elimination of water by interacting one of the carbonyl radicals per molecule of said dicarbonyl compound with a primary amino radical, said beta dicarbonyl compounds having the general formula



wherein R_1, R_2 and R_3 represent radicals selected from the group consisting of hydrogen, alkyl, aryl and aralkyl radicals containing a total of not more than 20 carbon atoms said reaction product being at least slightly soluble in said organic compound and said organic compound being susceptible to the deactivating action of said reaction product.

10. The method of prolonging the useful life of lubricating oil normally subject to deterioration through oxidation promoters selected from the group consisting of metallic iron, copper, chromium lead and compounds of copper, chromium and lead, comprising adding from time to time during use of the oil small amounts of a reaction product of an aliphatic poly primary amine having 2 to 12 carbon atoms with two mols of a beta dicarbonyl compound formed by the elimination of water by interacting not more than one of the carbonyl radicals of each molecule of the dicarbonyl compound with a primary amino radical, said beta dicarbonyl compounds having the general formula



wherein R_1, R_2 and R_3 represent radicals selected from the group consisting of hydrogen, alkyl, aryl and aralkyl radicals containing a total of not more than 20 carbon atoms said reaction product being at least slightly soluble in said lubricating oil.

11. The substance of claim 1 wherein said amino group is connected to an aromatic nucleus through an aliphatic linkage comprising at least 1 carbon atom.

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