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METAL DEACTIVATOR

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This invention relates to the stabilization of organic substances and particularly to the protection of organic substances against deterioration through oxidation catalyzed by the presence of certain metals. More particularly, it deals with improved industrial mineral hydrocarbons which, during their useful life, come in contact with metals capable of catalyzing oxidation.

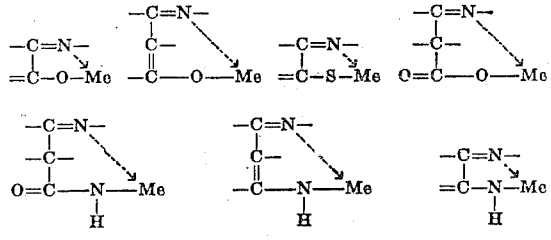
It is well known that organic substances normally contact metals and frequently contain small amounts of metals dissolved in the form of a soluble salt. It has been observed that the presence of such metals may have a detrimental effect on the stability of the organic substances. Inasmuch as bare traces of the metal may be very harmful and since the removal of these last traces is extremely difficult, it is often impossible to eliminate this troublesome catalyst of the oxidation reaction.

It has already been suggested to reduce the susceptibility of the organic substances to oxidation, induced by the presence of copper and other catalytically active metals, by adding to the organic substances certain deactivators which have the property of rendering the catalytic metals inactive. Among the deactivators heretofore suggested have been condensation products of aliphatic and aromatic primary polyamines with salicylaldehyde, benzoyl acetone, acetyl acetone, etc., aldoximes and ketoximes such as o-hydroxy naphthylaldoxime, salicylaldoxime, etc., and 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 as tested, for example, by the Voorhees-Eisinger method described in S. A. E. Journal 24, 584 (1929).

It is the purpose of this invention to provide deactivator compounds of improved effectiveness in reducing the catalytic effect of metal oxidation promoters, particularly copper, chromium, cobalt, lead and their compounds. It is another purpose to provide deactivators which, when added to organic substances, remain active for a considerable length of time when subjected to oxidizing influences.

An important application of this invention is as stabilizer for lubricating oils to retard discoloration, sludge formation, etc., due to catalytic oxidation during use when in contact with catalytic metals, particularly copper-containing bearings.

We have discovered that organo-metallic complexes of the catlytically inactive metals, lithium, beryllium, magnesium, calcium, strontium, barium, zinc, cadmium, aluminum and tin, with organic metal deactivators such as organic nitrogen-bearing compounds, which have a configuration such that the metal is a member of a five- or six-membered chelate ring, possess the property of deactivating certain metal oxidation catalysts, e. g., copper, lead, etc., and their compounds, thereby rendering them non-catalytic. The deactivating power of these metal complexes is considerably greater than that of the above organic compounds alone in the presence of solid metals. Suitable organic nitrogen-bearing compounds having a configuration such that the proper chelate ring is formed with the metal are those in which there is a polar radical capable of forming electrovalent metal compounds such as an acid-reacting group or an amine group capable of forming metal amides, separated from an aliphatic double-bonded trivalent nitrogen atom by at least two carbon atoms such that the total number of atoms in series from the nitrogen atom to the metal, inclusive, is 5 or 6. The acidic group may be —OH (in vicinal position to a double bond as in —COOH), —SH, —COSH, etc. It should preferably has a dissociation constant below 10^{-3}. Examples of such configurations are:



The effective configurations are characterized by the property of resonance. Resonance is considered to be the ability that certain molecules have of existing in an electronic state intermediate between two or more valence-bond structures that it is possible to write for the compound. The question of resonance is discussed in detail in Pauling, "Nature of the Chemical Bond."

The action of our deactivators appears to be specific for the oxidation catalyst metals enumerated above and their compounds.

Various classes of deactivators that may have the proper configuration are exemplified by the following: alkylated amino acetic acids, diphenylglyoxime, nitroso phenyl hydroxylamine, benzoinoxime, 2-hydroxy acetophenoxime, cyclohexanolonoxime, salicylaldoxime, 2-hydroxy-1-

naphthylidine - n - butylamine, 2 - hydroxy - 1 - naphthylidene-n-ethanolamine, 2 - hydroxy - 1 - naphthylidene diethylene triamine, hydro-(2-hydroxy-1-naphthylamide), salicylal ethanolamine, salicylal ethylamine, di-salicylal ethylene diamine, benzoyl acetonyl ethylene diamine, acetyl acetonyl ethylene diamine.

The complexes of this invention are effective in various normally liquid and normally solid liquefiable substantially neutral purely organic substances which are reasonably stable upon exposure to atmospheric oxygen under normal conditions of storage or use or both in the absence of active metal oxidation catalysts, but which oxidize in their presence; which substances are further free from metals except for small quantities of metal or metal compound contaminants such as may have been introduced during processing, manufacture, or normal use. 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, photographic developers, both natural and synthetic essential oils, perfumes, cellulose acetate, various resins, rubber, etc.

The amounts of complex 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 catalytic metal contained in the organic substance.

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.

If desired, a portion only of the organic deactivator need be in the form of its metal complex while the balance remains in the form of purely organic deactivator.

Solubility in hydrocarbon oils such as gasoline or lubricating oils of non-catalytic metal complexes of reaction products of primary diamines with salicyl or hydroxy aromatic aldehydes may be insufficient for dissolution of effective amounts, in which case it would be necessary to attach oil-solubilizing radicals to said reaction products or to the components going into the making of said products.

Effective oil-solubilizing radicals are, in general, aliphatic and cyclo-aliphatic hydrocarbon radicals possessing three or more carbon atoms, such as isopropyl, primary, secondary and tertiary butyl, etc., radicals; more than one solubilizing radical may be attached to the compound. More effective solubilizing radicals possess 6 or preferably 10 or more carbon atoms, such as hexyl, heptyl, octyl, iso-octyl, decyl, dodecyl, tetradecyl, cetyl, wax, etc., radicals; cyclo-aliphatic radicals such as cyclohexyl, methyl cyclohexyl, bicyclohexyl, C_{12} to C_{24} cyclo-aliphatic radicals as produced by hydrogenating corresponding condensation products of acetone, mesityl oxide, etc.

While solubility-in-oil requirements favor large solubilizing radicals, it is, on the other hand, desirable to keep these radicals to the minimum consistent with solubility to minimize the tendency of the radicals to reduce the deactivator effectiveness caused by steric hindrances. Further, it is desirable that the alkyl radical should contain not more than 12 carbon atoms in order to produce relatively low molecular weight compounds because the reaction between nitrogen components and the non-catalytic divalent metals, such as zinc and magnesium, is apparently one in which one mol of a nitrogen-bearing component, such as alkylated salicylal ethylene diamine, is capable of reacting with not more than one atom of the metal. It is not, therefore, desirable to add too great an amount of dead load to the molecule of the deactivator.

Our deactivators may be produced by any one of several well-known reactions. For example, an amine-aldehyde type deactivator may be prepared by the condensation of one mol of a primary diamine with two mols of hydroxy aromatic aldehydes under conditions such that one mol of aldehyde reacts with each primary amine group of the amine to produce an arylidene amine having an acidic hydroxy group attached to the aromatic nucleus. A metal complex of this condensation product may then be prepared by reacting the latter with a metal hydroxide. An alkylated complex, for example, the zinc complex of tetra isopropyl disalicylal ethylene diamine, may be prepared as follows:

1.1 mols of an alkylated hydroxy aromatic acid, e. g., di-isopropyl-salicylic acid, is dissolved with .56 mols of sodium carbonate in 2 liters of water and warmed until a clear solution is obtained. Then .6 mol of ethylene diamine is added followed by 5 mols of boric acid. Sodium amalgam is added to the mechanically stirred solution, care being taken to keep the solution faintly acidic by occasional additions of boric acid. After stirring for at least an hour the precipitate is filtered off and washed with water and dissolved in ether. The yellow ether solution is mixed with .25 mol of H_2SO_4 per mol of reacting alkylated aromatic acid and steam distilled. The distillate is made slightly alkaline with sodium carbonate and extracted with ether. The ether solution is evaporated and the resulting hydroxy aldehyde is a light brown oil. This aldehyde and ethylene diamine were dissolved separately in boiling ethanol and the hot solution of ethylene diamine added slowly to the boiling aldehyde solution. The reaction product appeared slowly as a yellow color in the solution and separated as a yellow crystalline product upon cooling. The yellow product was purified by recrystallization from a benzene solution.

The zinc complex of the condensation product is prepared by dissolving the ethylene diamine condensation product in alcohol and treating with an excess of zinc acetate in ethyl alcohol solution. The complex is advantageously recrystallized several times from ethyl alcohol to increase the purity of the product.

The following example illustrates the effectiveness of our deactivators:

Example

A sample of lubricating oil, S. A. E. 30 (Aeroshell 120), was divided into three portions. To each sample was added 2.2 $cm.^2$ copper surface per gram of oil in the form of copper wire. To the first sample was added 0.1*w*% of salicylal ethylene diamine, one of the best deactivators known but having a limited solubility in lubricating oils. To the second sample was added 0.4% of tetra isopropyl salicylal ethylene diamine, the isopropyl radical serving to impart greater solubility. To the third portion was added 0.15% of a zinc complex of tetra isopropyl

salicylal ethylene diamine. Each of the oils was then exposed to pure oxygen at atmospheric pressure and at a temperature of 150° C. Using the induction period of the oil containing salicylal ethylene diamine as the standard, the relative effectiveness of the other compounds was determined by dividing the induction period of the oil containing the particular additive by the induction period for the oil taken as standard. Results were as follows:

Compound	Induction period	Effectiveness ratio on basis of equimolal concentrations
0.1*w*% salicylal ethylene diamine (molality=0.0037 mols/1000 gr.)	*Minutes* 200	1.0
0.4*w*% tetra isopropyl salicylal ethylene diamine (molality=0.0094 mols/1000 gr.)	450	.52
0.15*w*% zinc complex of tetra isopropyl salicylal ethylene diamine (molality=0.0030 mols/1000 gr.)	560	4.1

It will be seen that the metal complex has a markedly superior deactivating effect over that of the organic deactivator alone.

The complex deactivators of this invention may be used in conjunction with other addition agents, for example, in gasolines together with anti-oxidants, or in lubricating oils together with anti-oxidants, blooming agents, anti-corrosives, E. P. compounds, etc. It is, however, desirable that the secondary 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 deactivators of this invention may be added to the organic substances to be stabilized in any desired form. They may be added as such or in a solution of a suitable solvent mixed with other addition agents, etc.

We claim as our invention:

1. A composition of matter consisting essentially of a substantially neutral purely organic substance which is normally stable but oxidizes when exposed to atmospheric oxygen in the presence of a copper oxidation catalyst, said substance having dissolved therein a small amount of a metal organo complex of an organic nitrogen-bearing deactivator for copper catalysts, said metal in said complex being non-catalytic and selected from the group consisting of lithium, beryllium, magnesium, calcium, strontium, barium, zinc, cadmium, aluminum and tin, said complex being soluble in said substance at least to the extent of .01% and having a configuration such that the non-catalytic metal is a member of a five- or six-membered chelate ring comprising at least two carbon atoms and at least one nitrogen atom which is trivalent, aliphatic and connected through a double bond to one of said carbons in said ring.

2. A composition of matter consisting essentially of a substantially neutral purely organic substance which is normally stable but oxidizes when exposed to atmospheric oxygen in the presence of a copper oxidation catalyst an added substance comprising an oxidation inhibiting amount of a metal organo complex of an organic nitrogen-bearing deactivator for copper catalysts, said metal in said complex being non-catalytic and selected from the group consisting of lithium, beryllium, magnesium, calcium, strontium, barium, zinc, cadmium, aluminum and tin, said complex being soluble in said substance at least to the extent of .01%, said deactivator containing a polar radical normally capable of forming with metals electrovalent compounds, said non-catalytic metal being attached to said polar radical and being separated from a nitrogen atom by at least two directly linked carbon atoms, the total number of atoms in series from said nitrogen atom to said non-catalytic metal, inclusive, being 5 or 6, said nitrogen atom being trivalent, aliphatic and connected through a double bond to one of said carbons in said ring.

3. The composition of claim 2, wherein said polar radical is an —OH radical in vicinal position to a double bond.

4. The composition of claim 2, wherein said polar radical is a carboxylic acid radical.

5. The composition of claim 2, wherein said polar radical is an amine radical capable of forming metal amides.

6. The composition of claim 2, wherein said substance is a hydrocarbon oil.

7. The composition of claim 2, wherein said substance is a refined lubricating oil.

8. The composition of claim 2, wherein the amount of said complex compound is between .01% and .10%.

9. A composition of matter consisting essentially of a substantially neutral pure organic substance which is normally stable when exposed to atmospheric oxygen, said matter containing as impurity an oxidation catalyst selected from the group consisting of copper, iron, chromium, cobalt, lead and their compounds in an amount sufficient to render said composition unstable toward atmospheric oxygen, and further containing dissolved an amount sufficient to deactivate said catalyst of a metal organo complex of an organic nitrogen-bearing deactivator for copper, said metal in said complex being non-catalytic and selected from the group consisting of lithium, beryllium, magnesium, calcium, strontium, barium, zinc, cadmium, aluminum and tin, said complex being soluble in said substance at least to the extent of .01%, said deactivator containing a polar radical normally capable of forming with metals electrovalent compounds, said non-catalytic metal being attached to said polar radical and being separated from a nitrogen atom by at least two directly connected carbon atoms, the total number of atoms in series from said nitrogen atom to said non-catalytic metal, inclusive, being 5 or 6, said nitrogen atom being trivalent, aliphatic and connected through a double bond to one of said carbons in said ring.

10. A hydrocarbon oil containing dissolved a stabilizing amount of a complex compound formed between an alkylated disalicylal ethylene di-imine and zinc.

11. A hydrocarbon oil containing dissolved a stabilizing amount of a complex compound formed between alkylated di-acetyl acetonyl ethylene di-imine and zinc.

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