Patented Apr. 18, 1944 2,346,663

UNITED STATES PATENT OFFICE

2,346,663

SUPPRESSION OF METAL CATALYSIS

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No Drawing. Application April 8, 1940, Serial No. 328,524

21 Claims. (Cl. 44—73)

This invention relates to a method for suppressing deterioration of olefin-containing hydrocarbon distillates such as results from the catalytic effect of metal compounds on oxidation reactions involving unsaturated hydrocarbons and resulting in the formation of gum.

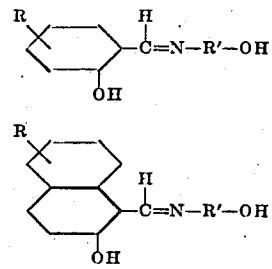
The use of gasoline gum inhibitors to prevent or minimize oxidation reactions resulting in the formation of objectionable peroxides, gums and other deleterious oxidation products has been practiced. They are particularly useful in cracked, reformed, and polymer gasolines which contain relatively high concentrations of monoolefins and somewhat smaller concentrations of other unsaturated hydrocarbons such as diolefins.

The function of inhibitors is primarily to minimize or prevent such oxidation reactions and thus keep the motor fuel in satisfactory condition for use in internal combustion engines. They tend to prevent losses in antiknock value which accompanies oxidation of this type of gasoline. Among the materials which have been used are various phenolic and amino compounds as well as fractions of wood tar oils, particularly those of hard woods, boiling in the range of approximately 240–280° C., etc., which are usually added to the gasoline in concentrations of approximately 0.001–0.1%, depending upon the effectiveness of the particular compound used and the gasoline to which it is added.

Although inhibitors are used in both treated and untreated gasolines, it is with the latter type that they find the greatest application. Treated gasolines are those which have been subjected to chemical refining processes such as sulfuric acid, fuller's earth and the like, either with or without a sweetening treatment following. Untreated gasolines are those which have received no refinement beyond possibly caustic washing and/or sweetening. The former type of gasoline is usually relatively stable and requires little or no added inhibitor, although the use of inhibitors has been practiced to supplement other refining methods. In the case of untreated gasolines, on the other hand, many of them are unstable and require the protection afforded by inhibitors to prevent undue deterioration during the time they are in storage.

Practically all gasolines require some form of sweetening treatment in order to improve the odor thereof and produce a product having a negative doctor test. The sodium plumbite or doctor process, as well as the hypochlorite sweetening process, have been used in the past with considerable success. During recent years, the so-called copper sweetening process has been developed in which gasoline is contacted with a copper-containing reagent. As a result of the presence of relatively minor amounts of impurities in such gasolines, the sweetened gasoline usually contains relatively small amounts of copper compounds which have a catalytic effect on oxidation reactions which may result when the gasoline comes in contact with air. Various methods have been developed for removing such copper compounds including treatment with alkali or alkaline earth metal sulfides and heavy metal sulfides such as zinc sulfide and the like. In some instances, however, these reagents may not be completely effective in removing the copper from the gasoline and as a consequence the gasoline may have a reduced stability and susceptibility to added gasoline gum inhibitors. Moreover, gasolines come in contact with various metals in the course of refining, storage and shipping operations, and this may result in the gasoline containing minute amounts of such metals as copper, iron, cobalt, nickel and the like, which are oxidation catalysts. It is with a method of preventing depreciation due to the presence of such catalysts that this invention is concerned.

In one specific embodiment the present invention comprises a method for suppressing the catalytic action of heavy metal compounds which may be contained in hydrocarbon distillates such as cracked gasoline and which tend to promote the formation of gum therein by adding to said gasoline approximately 0.0001–0.01% of a condensation product of an orthohydroxy aromatic aldehyde with a primary alkanol amine, either with or without an added gum inhibitor. Compounds of this type are represented by the following general formula:



wherein R may be hydrogen or a substituent group such as alkyl, aryl, hydroxyl, halogen, nitro, alkoxy, aryloxy or amino group, and wherein R' is an alkylene group. Representative compounds of this type are 2-hydroxy-1-naphthaldehyde-ethanolamine; o-hydroxy benzal-ethanolamine; 2-hydroxy-1-naphthaldehyde, 1-amino-1-propyl-2-pentanol; and o-hydroxy benzal-2 amino-2-methyl-1,3-propanediol.

The compounds of this invention, which are hereinafter termed suppressers, are not necessarily exactly equivalent. Furthermore they possess varying degrees of solubility in hydrocarbon distillate which may influence the effective-

ness in any given stock. The proper choice of a suppresser for any particular oil will depend upon these factors, and is, in the end, a matter of test.

In some cases the compounds may be used in the gasoline without added gum inhibitors. This is particularly true when used in connection with straight-run distillates or cracked gasolines which have been refined to an adequate degree of stability such as by acid-treatment or other suitable methods. However, these compounds are not of themselves gasoline gum inhibitors except to a minor extent, so that they do not result in a gasoline of improved stability except when metal compounds are present therein.

However, the usual method of application is to add both the suppresser and the gasoline gum inhibitor simultaneously. The resulting induction period is usually the same or slightly increased over that obtainable with the inhibitor alone in a gasoline free of metal compounds. The suppresser may be dissolved in the gasoline gum inhibitor. As a rule, smaller amounts of the suppresser are required than of the gum inhibitor, so that a relatively minor amount of the suppresser may be added to the inhibitor, say for example, less than 50% of the total mixture.

The following example is given to illustrate the usefulness of the invention, but should not be construed as limiting it to the compounds shown therein.

A Pennsylvania cracked gasoline containing 1 mg. of copper per liter of gasoline had an induction period of 35 minutes which increased upon the addition of 0.01% of N-butyl aminophenol to 85 minutes. When the various compounds of this invention were added to the inhibited gasoline in amounts of 0.01%, the induction period was increased as indicated in the following table. The induction period was measured by the well-known oxygen bomb induction period test method.

Suppresser	Per cent	Per cent N-butyl-amino-phenol	Oxygen bomb induc. period minutes
None	------	0.00	35
Do	------	0.01	85
o-Hydroxy-benzal-ethanolamine	0.01	0.01	200
2-hydroxy-1-naphthaldehyde ethanolamine	0.01	0.01	285
2-hydroxy-1-naphthaldehyde, 1 amino-1 propyl-2 pentanol	0.01	0.01	195
o-Hydroxy-benzal -2 amino -2 methyl 1,3,-propanediol	0.01	0.01	335

I claim as my invention:

1. A process for suppressing the catalytic effect of metal compounds on hydrocarbon distillate which comprises adding to said distillate a relatively minor portion of a condensation product of an orthohydroxy aromatic aldehyde and a primary alkanol amine.

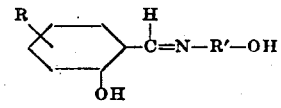
2. A process for suppressing the catalytic effect of metal compounds on gum formation in olefin-containing hydrocarbon distillate which comprises adding a relatively minor portion of a condensate product of an orthohydroxy mono-nuclear aromatic aldehyde and a primary alkanol amine.

3. A process for suppressing the catalytic effect of metal compounds on gum formation in olefin-containing hydrocarbon distillate which comprises adding to said distillate a relatively minor portion of a condensation product of an orthohydroxy poly-nuclear aromatic aldehyde and a primary alkanol amine.

4. A method of suppressing the catalytic effect of metal compounds on gum formation in olefin-containing distillate which comprises adding to said distillate a relatively minor portion of 2-hydroxy-1-naphthaldehyde-ethanolamine.

5. A method of suppressing the catalytic effect of metal compounds on gum formation in olefin-containing distillate which comprises adding thereto a relatively minor portion of a gum inhibitor and a second portion of a condensation product of an orthohydroxy aromatic aldehyde and a primary alkanol amine.

6. A process for suppressing the catalytic effect of metal compounds on gum formation in olefin-containing distillate which comprises adding thereto a compound having the following general formula:



wherein R is hydrogen or a substituent group and wherein R' is an alkylene group.

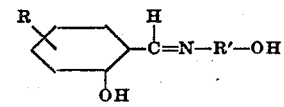
7. A process for suppressing the effect of metal compounds on gum formation in olefin-containing distillate which comprises adding to said distillate a condensation product of an orthohydroxy aromatic aldehyde with a primary alkanol amine in an amount within the limits of approximately 0.0001–0.01%.

8. An inhibitor of gum formation in cracked gasoline comprising essentially a mixture of a gasoline gum inhibitor with a condensation product of an orthohydroxy aromatic aldehyde and a primary alkanol amine.

9. An inhibitor of gum formation in cracked gasoline comprising essentially a mixture of a gasoline gum inhibitor with a condensation product of an orthohydroxy mono-nuclear aromatic aldehyde and a primary alkanol amine.

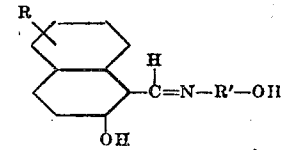
10. An inhibitor of gum formation in cracked gasoline comprising essentially a mixture of a gasoline gum inhibitor with a condensation product of an orthohydroxy poly-nuclear aromatic aldehyde and a primary alkanol amine.

11. An inhibitor of gum formation in cracked gasoline comprising essentially a mixture of a gasoline gum inhibitor with a condensation product of an orthohydroxy aromatic aldehyde and a primary alkanol amine having the general formula:



wherein R is hydrogen or a substituent group and wherein R' is an alkylene group.

12. An inhibitor of gum formation in cracked gasoline comprising essentially a mixture of a gasoline gum inhibitor with a condensation product of any orthohydroxy aromatic aldehyde and a primary alkanol amine having the general formula:



wherein R is hydrogen or a substituent group and wherein R' is an alkylene group.

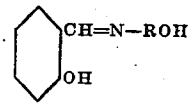
13. An inhibitor of gum formation in cracked

gasoline comprising essentially a mixture of a gasoline gum inhibitor with a relatively minor portion of 2-hydroxy-1-naphthaldehyde-ethanolamine.

14. A suppresser for the catalytic effect of metal compounds on gum formation in cracked gasoline which comprises a mixture of an N-substituted amino-phenol with a condensation product of an orthohydroxy aromatic aldehyde and a primary alkanol amine.

15. A suppresser for the catalytic effect of metal compounds on gum formation in cracked gasoline which comprises a mixture of a wood tar distillate gasoline gum inhibitor boiling within the range of approximately 240–280° C. and a condensation product of an orthohydroxy aromatic aldehyde with a primary alkanol amine.

16. Method of stabilizing gasoline containing traces of metallic compounds catalytically active to accelerate oxidation comprising adding thereto a small quantity of suppressor compound having the formula



where R is alkylene.

17. Method of stabilizing gasoline containing traces of metallic compounds catalytically active to accelerate oxidation comprising adding thereto a small amount of a hydroxy aromatic compound containing the radical CH=N—ROH directly atached to the aromatic ring and in which R is an alkylene group, the hydroxy group of the aromatic nucleus being in the ortho position with respect to said radical.

18. Motor fuel comprising olefinic gasoline and a relatively small amount of a condensation product of an orthohydroxy aromatic aldehyde and a primary alkanol amine.

19. Motor fuel comprising olefinic gasoline and a relatively small amount of an hydroxy aromatic compound containing the radical

CH=N—ROH

directly attached to the aromatic ring and in which R is an alkylene group, the hydroxy group of the aromatic nucleus being in the ortho position with respect to said radical.

20. Motor fuel comprising olefinic gasoline and relatively small amounts of a gum inhibitor and a condensation product of an orthohydroxy aromatic aldehyde and a primary alkanol amine.

21. Motor fuel comprising olefinic gasoline and relatively small amounts of a gum inhibitor and an hydroxy aromatic compound containing the radical CH=N—ROH directly attached to the aromatic ring and in which R is an alkylene group, the hydroxy group of the aromatic nucleus being in the ortho position with respect to said radical.

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