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SUPPRESSION OF METAL CATALYSIS

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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.

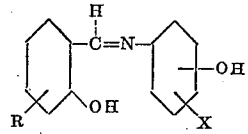
The function of inhibitors is primarily to minimize or prevent such oxidation reactions and thus keep the motor fuel in satisfactory condition for use in internal combustion engines. They tend to prevent losses in antiknock value which accompanies oxidation of this type of gasoline. Among the materials which have been used are various phenolic, amino, and amino-phenolic compounds as well as fractions of wood tar oil, 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 may be defined as those which have been subjected to chemical refining processes such as sulfuric acid, fuller's earth, and the like, either with or without a subsequent sweetening treatment. Untreated gasolines may be said to be 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, storing 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 gasolines 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 a mono- or polyhydroxy benzaldehyde with an aminophenol, either with or without a gasoline gum inhibitor.

Compounds of this type may be represented by the general formula:



wherein R is a substituent group such as an hydroxyl group, a hydrogen atom or an alkyl group substituted in any position in the ring. In the aminophenol group, the hydroxyl group may be in any position in the ring, which furthermore may be substituted by an additional group represented by X which may be an alkyl group, an hydroxyl group or a hydrogen atom. A representative compound of this type is ortho-hydroxy-benzal-ortho-aminophenol.

These compounds may be made by dissolving

the components in alcohol, mixing the alcoholic solutions, and warming the mixture. The product is purified by recrystallization.

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 effectiveness in any given stock and the proper choice of a suppresser for any particular oil will depend upon these factors.

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. When using inhibitors of the aminophenol type, the hydroxy-benzaldehyde in alcoholic solution can be added directly to the inhibitor.

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

Example 1

A cracked gasoline produced by cracking Pennsylvania crude oil was sweetened by a copper-sweetening method and was found to contain 1 mg. of copper per liter of gasoline. The induction period when the copper was completely removed was approximately 100 minutes and with the copper present was approximately 40 minutes. By adding 0.001% of ortho-hydroxybenzal-ortho-aminophenol, the induction period was increased to 90 minutes. When adding 0.01% of a commercial gum inhibitor to the copper-containing gasoline without a suppresser present, the induction period was 150 minutes. When using the 0.01% of the inhibitor together with 0.001% of the suppresser, the induction period was 400 minutes. This compared with an induction period of 325 minutes for a copper-free sample of the gasoline plus 0.01% of the commercial inhibitor.

Example 2

To an acid-treated cracked gasoline having an induction period of 300 minutes and a copper-dish gum content of 5 mg., was added 1.5 mg. of copper per liter of gasoline. The induction period was reduced to 100 minutes and the copper dish gum content increased to 95. Addition of 0.001% of ortho-hydroxy-benzal-ortho-aminophenol to the gasoline brought the induction period to 325 minutes, the gum content to 15 mg. per 100 cc.

Example 3

A Mid-Continent gasoline containing 0.75 mg. of copper per liter had an induction period upon the addition of a commercial gum inhibitor of 175 minutes. Upon the addition of 0.005% of ortho-hydroxy-benzal-meta-aminophenol, the induction period was increased to 275 minutes.

Another sample was treated with 2,4-dihydroxy-benzal ortho-aminophenol and the induction period in the presence of a commercial gum inhibitor was increased to 300 minutes.

Example 4

The Pennsylvania gasoline referred to in Example 1 was treated with 0.004% of 2,4-dihydroxy-benzal para-aminophenol. The induction period was increased to 370 minutes.

Upon the addition of orthohydroxy-benzal-para-aminophenol to the gasoline containing the commercial inhibitor, an induction period of 250 minutes was obtained.

I claim as my invention:

1. A method for treating gum-forming hydrocarbon distillates containing metal compounds having a catalytic effect on gum formation, which comprises incorporating into the distillate a relatively small but sufficient quantity of an ortho-hydroxybenzal-aminophenol to suppress said catalytic effect of the metal compounds.

2. A method for treating gum-forming hydrocarbon distillates containing metal compounds having a catalytic effect on gum formation, which comprises incorporating into the distillate a relatively small but sufficient quantity of a mono-ortho-hydroxybenzal-aminophenol to suppress said catalytic effect of the metal compounds.

3. The method as defined in claim 1 further characterized in that the suppressor of said catalytic effect comprises ortho-hydroxybenzal-ortho-aminophenol.

4. The method as defined in claim 1 further characterized in that the suppressor of said catalytic effect comprises ortho-hydroxybenzal-meta-aminophenol.

5. The method as defined in claim 1 further characterized in that the suppressor of said catalytic effect comprises ortho-hydroxybenzal-para-aminophenol.

6. The method as defined in claim 1 further characterized in that the suppressor of said catalytic effect is incorporated into the distillate in the amount of about 0.0001 to 0.01%.

7. Motor fuel comprising gum-forming gasoline containing metal compounds having a catalytic effect on gum formation and additionally containing, as a suppressor of said catalytic effect, a relatively small amount of an ortho-hydroxy-benzal-amino-phenol.

8. Motor fuel comprising gum-forming gasoline containing metal compounds having a catalytic effect on gum formation and additionally containing, as a suppressor of said catalytic effect, a relatively small amount of a mono-ortho-hydroxybenzal-aminophenol.

9. Motor fuel comprising gum-forming gasoline containing metal compounds having a catalytic effect on gum formation and additionally containing, as a suppressor of said catalytic effect, a relatively small amount of ortho-hydroxybenzal-ortho-aminophenol.

10. Motor fuel comprising gum-forming gasoline containing metal compounds having a catalytic effect on gum formation and additionally containing, as a suppressor of said catalytic effect, a relatively small amount of ortho-hydroxybenzal-meta-aminophenol.

11. Motor fuel comprising gum-forming gasoline containing metal compounds having a cata-

lytic effect on gum formation and additionally containing, as a suppressor of said catalytic effect, a relatively small amount of ortho-hydroxybenzal-para-aminophenol.

12. Motor fuel comprising gum-forming gasoline containing metal compounds having a catalytic effect on gum formation and additionally containing, as a suppressor of said catalytic effect, about 0.0001 to 0.01% of an ortho-hydroxybenzal-aminophenol.

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