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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 mono-olefins and somewhat smaller concentrations of other unsaturated hydrocarbons such as diolefins.

The function of inhibitors is primarily to minimize or prevent such oxidation reaction 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 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.

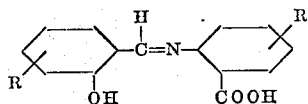
Although inhibitors are used in both treated and untreated gasolines, it is with the latter type that they find the greatest application. Treated gasolines are those which have been subjected to chemical refining processes such as sulfuric acid, fuller's earth, and the like, either with or without a 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, has 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 effect 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 anthranilic acid either with or without a gasoline gum inhibitor.

Compounds of this type may be designated by the general formula



wherein R and R' may be hydroxyl groups, alkyl groups, or hydrogen atoms. The compounds are prepared by mixing alcoholic solutions of a suitable orthohydroxy benzaldehyde with anthranilic acid or a substituted anthranilic acid. The mass may then be warmed and the resulting compound recrystallized from an alcoholic solution if a further degree of purity is needed.

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

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

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 distillate 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 at most, so that they do not result in a gasoline of improved stability except when metal compounds are present therein.

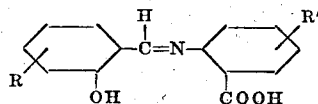
However, the usual method of application is to add both the suppressor and the gasoline gum inhibitor simultaneously. The resulting induction period is usually the same or slightly increased over that obtainable with the inhibitor alone in a gasoline free of metal compounds. The suppressor may be dissolved in the gasoline gum inhibitor. As a rule, smaller amounts of the suppressor are required than of the gum inhibitor so that a relatively minor amount of the suppressor 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. Among others the inhibitors include N-substituted aminophenols and wood tar distillate fractions boiling in the range of approximately 240-280° C.

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

A Mid-Continent cracked gasoline which contained 1 mg. of copper per liter of gasoline had an induction period of 55 minutes which increased to 75 minutes upon the addition of 0.01% of commercial gum inhibitor. When 0.01% of orthohydroxy benzal anthranilic acid was added to the gasoline containing the commercial gum inhibitor, the induction period was increased to 250 minutes. Addition of the orthohydroxy benzal anthranilic acid to the gasoline without the commercial gum inhibitor increased the induction period to 100 minutes.

I claim as my invention:

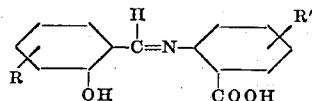
1. A process for suppressing the catalytic effect of metal compounds on gum formation in olefin-containing hydrocarbon distillate which comprises adding to said distillate a relatively minor portion of a compound having the general formula



wherein R and R' are substituent alkyl groups, hydroxyl groups or hydrogen atoms.

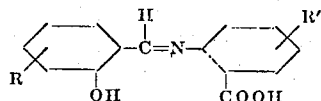
2. A method of suppressing the catalytic effect of metal compounds on gum formation in olefin-containing hydrocarbon distillate which comprises adding to said distillate a relatively minor portion of orthohydroxy benzal anthranilic acid.

3. Olefinic distillate containing, as a suppressor for the catalytic action of metal compounds on gum formation, a compound having the general formula



wherein R and R' are alkyl groups, hydroxyl groups or hydrogen atoms.

4. Olefinic gasoline containing, as a suppressor for the catalytic action of metal compounds on gum formation, a compound having the general formula



wherein R and R' are alkyl groups, hydroxyl groups or hydrogen atoms.

5. Olefinic distillate containing, as a suppressor for the catalytic action of metal compounds on gum formation, orthohydroxy benzal anthranilic acid.

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