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STABILIZATION OF MOTOR FUELS

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17 Claims. (Cl. 44—9)

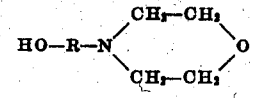
This invention relates to the stabilization of motor fuels comprising cracked hydrocarbon spirits such as cracked gasoline and motor benzol.

It is well known that motor fuels comprising cracked hydrocarbon spirits normally tend to form gummy and resinous products upon storage, which products are highly objectionable. Cracked gasoline particularly is subject to this form of deterioration. Also, motor fuels such as motor benzol are produced containing cracked hydrocarbon spirits which also tend to form gummy and resinous products.

Motor fuels comprising cracked hydrocarbon spirits have been treated by various means to remove the cracked spirits. This has been found to be objectionable for motor fuels to be used in present day automotive internal combustion engines. Accordingly, it has been suggested to add to such motor fuels various compounds which will inhibit or retard the formation of gummy and resinous products. The most common type of compounds, which have been employed for this purpose, are the phenolic and amino compounds. The phenolic type of compounds have generally been preferred because the amino type usually discolor the motor fuel or accelerate discoloration thereof. The phenolic type of compound, however, is generally objectionable due to its low solubility and its corrosive characteristics. It has been proposed to employ amino hydroxy compounds to obtain the advantages of both the phenolic and amino compounds without their disadvantages. This last expedient has not proved to be entirely satisfactory as the amino phenols, such as para-amino-phenol, are insufficiently soluble in the gasoline and also tend to discolor upon storage. It has been proposed to employ substituted amino-phenols in order to overcome the disadvantages of compounds such as para-amino-phenol. This last expedient has met with some degree of success. However, these latter compounds, as a general rule, tend to discolor the motor fuel on storage to some extent over extended periods of time.

An object of the present invention is to provide new compounds to be employed for stabilizing motor fuels comprising cracked hydrocarbon spirits which compounds are exceedingly effective for preventing the formation of gum in the motor fuels and do not discolor the motor fuels during storage. A further object is to provide improved methods for stabilizing motor fuels comprising cracked hydrocarbon spirits. Another object is to provide motor fuels comprising cracked hydrocarbon spirits which do not discolor and in which the tendency to form gum is greatly inhibited. Still other objects are to provide new compositions of matter and to advance the art. Other objects will appear hereinafter.

These objects may be accomplished in accordance with our invention which comprises incorporating in motor fuels comprising cracked hydrocarbon spirits, such as cracked gasoline and motor benzol, a compound of the type:



wherein R represents an aryl nucleus, such as phenyl, naphthyl, diphenyl, and the like, which may or may not contain substituents. When the aryl nucleus is substituted, the substituents may be alkyl, alkaryl or aryl hydrocarbon radicals, such as methyl, ethyl, propyl, butyl, amyl, benzyl, methyl benzyl, phenyl ethyl, phenyl, naphthyl and the like. By the term alkaryl as employed herein, it will be understood that we mean an aliphatic hydrocarbon group in which at least one hydrogen is substituted by an aryl nucleus. Among the compounds which we have found to be particularly satisfactory for our purpose are p-hydroxy N-phenyl morpholine, 4-hydroxy-2-methyl-N-phenyl morpholine and 4-hydroxy-3-methyl-N-phenyl morpholine. Methods of making compounds of this type are disclosed in the patent to Horace B. Pray, No. 2,063,191. Briefly, the hydroxy aryl morpholines are prepared by heating an aminophenol with beta beta' dichlor ethyl ether in the presence of water and a mild inorganic alkali such as magnesium hydroxide, magnesium oxide, calcium carbonate, zinc oxide and the like under slight superatmospheric pressure. The hydroxy aryl morpholine obtained will be the one corresponding with the aminophenol employed. These compounds are insoluble in water and will precipitate from the solution and can be easily separated therefrom.

The effectiveness of these compounds as antigumming agents was tested essentially according to the method proposed by Voorhees and Essinger in J. S. A. E. 24, 584 (1929). In this test, 100 cc. of the motor fuel is heated in a glass flask under an oxygen atmosphere at 100° C. The flask is connected to a mercury manometer and the pressure observed at regular intervals. The elapsed time, from the start of the test until the motor fuel begins to absorb oxygen, as shown by the fall of the pressure, is known as the "induction period" of the fuel. The effectiveness of an antigumming agent or gum inhibitor is measured by the increase in the induction period caused by the addition of a known amount of inhibitor. That the induction period is directly related to gum formation can be shown by heating a control sample of gasoline, containing no inhibitor, beyond its induction period and a second sample of gasoline, containing the inhibitor, for the same length of time and determining the gum

formed in each case by evaporating the gasoline samples in tared dishes in an inert atmosphere. The residue is the gum formed in each case.

As is well known to those skilled in the art, p-aminophenol, under the above test conditions, gives very satisfactory results. The use of this compound is not, however, commercially practical since its solubility, at ordinary temperatures, is insufficient to permit the use of a sufficient amount of the compound. Moreover, gasoline, containing p-aminophenol, is rapidly discolored under the action of light and air.

We have now found that the hydroxy N-aryl morpholines and particularly the p-hydroxy N-phenyl morpholines and the o-hydroxy N-phenyl morpholines are free from these disadvantages. Their solubility in gasoline is sufficient to permit the use of the quantity required to give an effective stabilization of the gasoline and their solutions in gasoline do not become colored during storage over extended periods of time.

In order to more clearly illustrate our invention and the advantageous results to be obtained thereby, the following examples are given:

Example 1

A gum-free unsaturated gasoline, containing 0.002% by weight of p-hydroxy N-phenyl morpholine, had an induction period of 270 minutes, when subjected to the above described test. A control sample of the same gasoline, containing no inhibitor, had an induction period of only 60 minutes, under the same conditions.

Example 2

A gum-free unsaturated gasoline, containing 0.003% by weight of p-hydroxy N-phenyl morpholine, had an induction period of 460 minutes, as determined by the above test. The control sample, without inhibitor, had an induction period of only 60 minutes.

During this last test, samples of gasoline were withdrawn at the end of 240 minutes and evaporated in a steam oven in tared dishes. The weight of gum, obtained from the uninhibited sample, was 246 mg. from 25 cc. of gasoline. The weight of gum, obtained from the inhibited sample, was 3 mg. from 25 cc. of gasoline.

Example 3

A gum-free unsaturated gasoline, containing 0.003% by weight of 4-hydroxy-2-methyl-N-phenyl morpholine, had an induction period of 130 minutes. The control sample gave 70 minutes, under the same conditions.

Example 4

A gum-free unsaturated gasoline, containing 0.003% by weight of 4-hydroxy-3-methyl-N-phenyl morpholine, had an induction period of 570 minutes. By the same test, the uninhibited gasoline had an induction period of only 70 minutes.

Other compounds of the class which may be employed with like results are: 4-hydroxy-2-ethyl-N-phenyl morpholine, 4-hydroxy-3-butyl-N-phenyl morpholine, 4-hydroxy-3-isopropyl-N-phenyl morpholine, 4-hydroxy-2-benzyl-N-phenyl morpholine.

The p-hydroxy-N-phenyl morpholines containing hydrocarbon radicals substituted in the morpholine nucleus and the 2-hydroxy N-phenyl morpholines should also be mentioned. Other compounds within the class which may be mentioned are: 4-methyl-2-hydroxy-N-phenyl morpholine, 3-butyl-2-hydroxy-N-phenyl morpholine, 4-hydroxy-N-phenyl-3'-5'-dimethyl morpholine.

The aryl group may also contain 2 or 3 hydrocarbon substituents which may be alike or different.

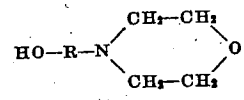
The amounts of the gum inhibitors, which it is necessary to employ, will vary with the nature and concentration of the unsaturated constituents of the motor fuel and the degree of stabilization it is desired to obtain. In general, however, the concentration of inhibitor in the motor fuel will be substantially less than 0.1% by weight.

From all of the above, it will be apparent that we have discovered a new class of compounds which are very efficient gum inhibitors, which are sufficiently soluble in gasoline to be readily utilized, and which do not cause noticeable discoloration of the motor fuel in aging.

While we have disclosed certain specific embodiments of our invention and the preferred modes of carrying the same into effect, it will be readily apparent to those skilled in the art that many variations and modifications may be made therein without departing from the spirit of our invention. Accordingly, the scope of our invention is to be limited solely by the appended claims construed as broadly as is permissible in view of the prior art.

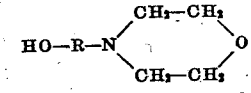
We claim:

1. Motor fuel comprising cracked hydrocarbon spirits normally tending to form gummy substances on storage having incorporated therein, in an amount sufficient to inhibit the formation of the gummy substances, a compound of the type:



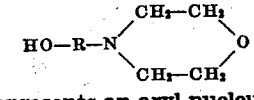
wherein R represents an aryl nucleus.

2. Motor fuel comprising cracked hydrocarbon spirits normally tending to form gummy substances on storage having incorporated therein, in an amount sufficient to inhibit the formation of the gummy substances, a compound of the type:



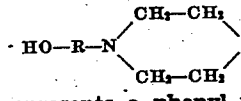
wherein R represents a phenyl nucleus.

3. Motor fuel comprising cracked hydrocarbon spirits normally tending to form gummy substances on storage having incorporated therein, in an amount sufficient to inhibit the formation of the gummy substances, a compound of the type:



wherein R represents an aryl nucleus having substituted therein at least one member of the group consisting of alkyl, alkaryl and aryl groups.

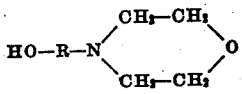
4. Motor fuel comprising cracked hydrocarbon spirits normally tending to form gummy substances on storage having incorporated therein, in an amount sufficient to inhibit the formation of the gummy substances, a compound of the type:



wherein R represents a phenyl nucleus having substituted therein at least one member of the

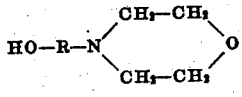
group consisting of alkyl, alkaryl and aryl groups.

5. Motor fuel comprising cracked hydrocarbon spirits normally tending to form gummy substances on storage having incorporated therein, in an amount sufficient to inhibit the formation of the gummy substances, a compound of the type:



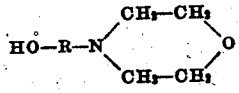
wherein R represents an aryl nucleus and wherein the hydroxy group is para to the morpholine radical.

6. Motor fuel comprising cracked hydrocarbon spirits normally tending to form gummy substances on storage having incorporated therein, in an amount sufficient to inhibit the formation of the gummy substances, a compound of the type:



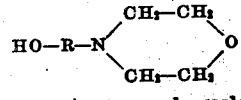
wherein R represents a phenyl nucleus and wherein the hydroxy group is para to the morpholine radical.

7. Motor fuel comprising cracked hydrocarbon spirits normally tending to form gummy substances on storage having incorporated therein, in an amount sufficient to inhibit the formation of the gummy substances, a compound of the type:



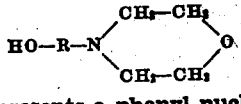
wherein R represents a phenyl nucleus having substituted therein at least one member of the group consisting of alkyl, alkaryl and aryl groups and wherein the hydroxy group is para to the morpholine radical.

8. Cracked gasoline normally tending to form gummy substances on storage having incorporated therein, in an amount sufficient to inhibit the formation of the gummy substances, a compound of the type:



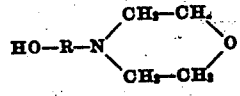
wherein R represents an aryl nucleus.

9. Cracked gasoline normally tending to form gummy substances on storage having incorporated therein, in an amount sufficient to inhibit the formation of the gummy substances, a compound of the type:



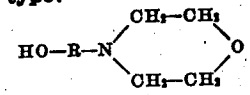
wherein R represents a phenyl nucleus.

10. Cracked gasoline normally tending to form gummy substances on storage having incorporated therein, in an amount sufficient to inhibit the formation of the gummy substances, a compound of the type:



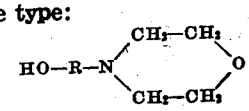
wherein R represents an aryl nucleus having substituted therein at least one member of the group consisting of alkyl, alkaryl and aryl groups.

11. Cracked gasoline normally tending to form gummy substances on storage having incorporated therein, in an amount sufficient to inhibit the formation of the gummy substances, a compound of the type:



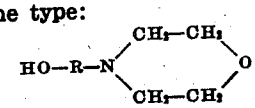
wherein R represents a phenyl nucleus having substituted therein at least one member of the group consisting of alkyl, alkaryl and aryl groups.

12. Motor benzol normally tending to form gummy substances on storage having incorporated therein, in an amount sufficient to inhibit the formation of the gummy substances, a compound of the type:



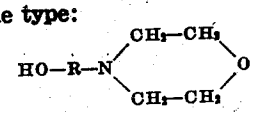
wherein R represents an aryl nucleus.

13. Motor benzol normally tending to form gummy substances on storage having incorporated therein, in an amount sufficient to inhibit the formation of the gummy substances, a compound of the type:



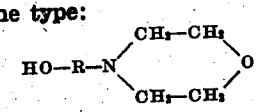
wherein R represents a phenyl nucleus.

14. Motor benzol normally tending to form gummy substances on storage having incorporated therein, in an amount sufficient to inhibit the formation of the gummy substances, a compound of the type:



wherein R represents an aryl nucleus having substituted therein at least one member of the group consisting of alkyl, alkaryl and aryl groups.

15. Motor benzol normally tending to form gummy substances on storage having incorporated therein, in an amount sufficient to inhibit the formation of the gummy substances, a compound of the type:



wherein R represents a phenyl nucleus having substituted therein at least one member of the group consisting of alkyl, alkaryl and aryl groups.

16. Gasoline containing cracked gum forming hydrocarbon compounds and a para hydroxy N phenyl morpholine compound in small quantity sufficient to inhibit gum formation therein.

17. A motor fuel comprising cracked gasoline normally tending to form gummy substances on storage and having incorporated therein para hydroxy N-phenyl morpholine in an amount sufficient to retard the formation of said gummy substances.

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