

UNITED STATES PATENT OFFICE

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DETERIORATION INHIBITORS FOR A HYDROCARBON MOTOR FUEL

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This invention relates to the treatment of hydrocarbon motor fuels and more particularly to the incorporation in the motor fuels of substances, known as inhibitors or antioxidants, which act to retard deterioration of the motor fuels.

It is known that hydrocarbon motor fuels produced in the cracking of petroleum have an undesirable tendency to undergo deterioration on storage, with loss in such valuable properties as light color, low gum content and anti-knock value, the deterioration being due principally to oxidation and being accelerated by the photochemical action of light. Straight-run gasolines, on the other hand, do not ordinarily have the same undesirable tendency to deteriorate, although blended stocks containing cracked gasoline and straight-run gasoline usually show the undesirable tendency to deteriorate. Similar fractions of hydrocarbon distillates produced by the deterioration of hydrocarbonaceous materials, other than petroleum, frequently also show a tendency to deteriorate upon storage.

It has been found that such deterioration of hydrocarbon motor fuels can be retarded to a greater or lesser degree by incorporating in the motor fuel certain phenols, certain aminophenols, certain aminophenol derivatives in which at least one hydrogen atom of the amino group of the aminophenol is replaced by an alkyl, an aralkyl or a cycloalkyl group, certain phenylenediamines or certain phenylenediamine derivatives in which at least one hydrogen atom of at least one of the amino groups of the phenylenediamine is replaced by an alkyl, an aralkyl or a cycloalkyl group. The majority of such inhibitors are solid substances which, at best, dissolve but slowly in motor fuels.

From the practical standpoint of handling motor fuels during the treatment thereof with inhibitors, it is usually most desirable to feed the inhibitor continuously or intermittently into the flow of the fuel. However, the aforesaid solid inhibitors do not ordinarily rapidly dissolve and distribute themselves uniformly throughout the motor fuel when incorporated in this manner. For this reason it has been proposed to employ mobile solutions of the inhibitors which can be fed into the flow of the motor fuel.

A number of solvents have been proposed for this purpose. Certain solvents may be especially useful with one type of inhibitor, but of much smaller utility with other types of inhibitors. For example, for N-alkyl-p-aminophenols, low molecular weight alcohols, such as methyl, ethyl,

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n-propyl, isopropyl, n-butyl, isobutyl or secondary butyl alcohol are suitable. A particularly good solvent is a mixture consisting of from 10 to 20 per cent by volume of methyl alcohol and from 90 to 80 percent of isopropyl alcohol. On the other hand, for N,N'-di secondary alkyl-p-phenylenediamines, the alcohols are less suitable. In this case, low molecular weight ketones, such as acetone or ethyl methyl ketone are much more suitable. In still other cases, ethers, such as diethyl ether or diisopropyl ether are of particular utility, or esters, such as methyl acetate, or aromatic hydrocarbons, such as benzene, toluene, or the xylenes are suitable, or ether-alcohols, such as β -methoxyethyl alcohol or β -ethoxyethyl alcohol are suitable.

It has been found that with certain solvents, certain inhibitors tend to develop color, more than they do with other solvents. Moreover, solutions of certain inhibitors in certain solvents tend to become troublesomely viscous or the inhibitors separate from the solution at very low temperatures, e. g. of the order of -40° F.

The problem of the inhibitor solution developing color is especially troublesome. Even with the best solvents which are known for a particular inhibitor, color tends to develop in the inhibitor solution in a relatively short period of time. We have now found that this development of color in inhibitor solutions can be retarded and in some cases practically eliminated by reducing the oxygen content of the solvent to not more than 8 parts per million. With certain combinations of inhibitor and solvent containing not more than 8 parts per million of dissolved oxygen, very marked improvement has been obtained, while in other combinations, the improvement is not as great. For example, in a combination of N,N'-diisopropyl-p-phenylenediamine with acetone containing not more than 8 parts per million of dissolved oxygen, an inhibitor solution which remains colorless for an extended period of time is obtained. On the other hand, in a combination of this same phenylenediamine derivative with methyl alcohol, the color improvement is not as great. Likewise, with a combination of N-(n-primary butyl)-p-aminophenol and isopropyl alcohol containing not more than 8 parts per million of dissolved oxygen, an inhibitor solution which does not develop color for an extended period of time is obtained. The same is true for a solution of N-(n-primary butyl)-p-aminophenol in a solvent mixture consisting of from 10 to 20 per cent by volume of methyl alcohol and from 90 to 80 per cent by volume of iso-

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propyl alcohol, said solvent mixture containing not more than 8 parts per million of dissolved oxygen. Likewise, we have found that any organic solvent containing not more than 8 parts per million of dissolved oxygen in combination with any inhibitor of the aforesaid classes is more resistant to the development of color than are combinations made up of solvents containing larger amounts of dissolved oxygen.

Organic solvents containing not more than 8 parts per million of dissolved oxygen can be prepared by purging the organic solvent of dissolved oxygen by passing an inert gas, such as carbon dioxide, nitrogen, methane or ethane through the organic solvent until the dissolved solvent is substantially displaced, or the organic solvent can be boiled to remove the dissolved oxygen or the solvent can be distilled. In practice a large tank of organic solvent holding several thousand gallons can be purged of oxygen by passing carbon dioxide through the solvent and then storing the purged solvent in an atmosphere of carbon dioxide until ready for use. The carbon dioxide is introduced through an entrance in the bottom of the tank under a pressure of 20 pounds per square inch. While the gas is bubbling through the solvent, the solvent is advantageously agitated. Agitation can be accomplished by means of a circulating pump. Twelve hours is usually sufficient to purge such solvents as methyl alcohol, isopropyl alcohol, acetone or methyl acetate.

The following examples are offered to illustrate typical solutions which I employ in practicing my invention.

Example I

	Grams
Isopropyl alcohol (not more than 8 P. P. M. of oxygen) -----	25
Methyl alcohol (not more than 8 P. P. M. of oxygen) -----	5
N - monobenzyl - p - aminophenol -----	25

Example II

Isopropyl alcohol (not more than 8 P. P. M. of oxygen) -----	25
Methyl alcohol (not more than 8 P. P. M. of oxygen) -----	5
N - (n - primary butyl) - p - aminophenol -----	25

Example III

Isopropyl alcohol (not more than 8 P. P. M. of oxygen) -----	25
Ethyl alcohol (not more than 8 P. P. M. of oxygen) -----	5
N - (n - primary butyl) - p - aminophenol -----	25

Example IV

β -methoxyethyl alcohol (not more than 8 P. P. M. of oxygen) -----	30
N,N'-diisopropyl - p - phenylenediamine -----	25

Example V

Acetone (not more than 8 P. P. M. of oxygen) -	30
N,N'-diisopropyl - p - phenylenediamine -----	30

Ordinarily, I have found it advantageous to make up the solutions of inhibitors in my new solvents, employing about one part by weight of the inhibitor to one by weight of the solvent. Other ratios of solvent to inhibitor can be employed.

Sufficient of the solution of the inhibitor should be incorporated in the gasoline to give a concentration of inhibitor in the gasoline which will substantially retard deterioration of the gasoline.

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Ordinarily a concentration of inhibitor of from about 0.01 g. to about 1.0 g. per 1,000 g. of motor fuel, i. e. from about 0.001 per cent to about 0.1 per cent by weight will suffice. The most useful and economical concentration of inhibitor will, of course, vary from inhibitor to inhibitor and motor fuel to motor fuel. The most advantageous concentration of inhibitor is, of course, readily determined by making the ordinary tests and observations customarily employed in the art.

As phenolic inhibitors, hydroquinone, C,C-diamyl-hydroquinone, α -naphthol and C-tertiary butyl catechol are exemplary. As inhibitors which are derivatives of aminophenols, the following are exemplary: N-methyl-p-aminophenol, N-ethyl-p-aminophenol, N-(n-propyl)-p-aminophenol, N-isopropyl-p-aminophenol, N-(n-primary butyl)-p-aminophenol, N-isobutyl-p-aminophenol, N-iscamyl-p-aminophenol, N-(n-primary amyl)-p-aminophenol, N-methyl-C-isopropyl-p-aminophenol, N-hexyl-p-aminophenols, N-octyl-p-aminophenols and N-cetyl-p-aminophenol, N-methyl-N-(n-primary butyl)-p-aminophenol, N-benzyl-p-aminophenol and N-cyclohexyl-p-aminophenol. As inhibitors which are derivatives of phenylene-diamines, the following are exemplary: N,N'-diisopropyl-p-phenylenediamine, N,N'-di-secondary butyl-p-phenylenediamine, N,N'-dimethyl-p-phenylenediamine, N,N'-dicyclohexyl-p-phenylenediamine, N,N'-di-2-amyl-p-phenylenediamine, N,N'-di-3-amyl-p-phenylenediamine, N,N'-dibenzyl-p-phenylenediamine. Mixtures of the inhibitors of this application can be employed. However, the complex condensation products claimed in United States Patent No. 2,163,639, dated June 27, 1939, in combination with organic solvents containing not more than 8 parts per million of oxygen are not to be regarded as included within this application nor within the scope of the claims forming a part of this application or any patent issuing hereon.

Dissolved oxygen in organic solvents can be determined by the indigo carmine method described at pages 137-138 in "Colorimetric Methods of Analyses" by Snell and Snell, 1936, D. Van Nostrand Company, Inc.

What I claim as my invention and desire to be secured by Letters Patent of the United States is:

1. A deterioration inhibitor for a hydrocarbon motor fuel comprising a solution in an organic solvent selected from the group consisting of alcohols containing from one to four carbon atoms, mixtures of said alcohols, and ketones containing from 3 to 4 carbon atoms, of at least one inhibitor selected from the group consisting of N-alkyl-p-aminophenols in which the alkyl group contains from 1 to 5 carbon atoms and N,N'-dialkyl-p-phenylenediamines in which each alkyl group contains from 1 to 5 carbon atoms, said organic solvent containing not more than 8 parts per million of dissolved oxygen.

2. A deterioration inhibitor for cracked gasoline comprising a solution in an alcohol containing from one to four carbon atoms of a N-(n-primary butyl)-p-aminophenol inhibitor which retards deterioration of cracked gasoline, said alcohol containing not more than 8 parts per million of dissolved oxygen.

3. A deterioration inhibitor for cracked gasoline comprising a solution in a mixture of from 90 to 80 per cent by volume of isopropyl alcohol and 10 to 20 per cent by volume of methyl alcohol of N-(n-primary butyl)-p-aminophenol,

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said mixture of alcohols containing not more than 8 parts per million of dissolved oxygen.

4. A deterioration inhibitor for cracked gasoline comprising a solution in a ketone containing from three to four carbon atoms of a N,N'-dialkyl-p-phenylenediamine inhibitor which retards deterioration of cracked gasoline, said ketone containing not more than 8 parts per million of dissolved oxygen.

5. A deterioration inhibitor for cracked gasoline comprising a solution in a ketone containing from three to four carbon atoms of N,N'-diisopropyl-p-phenylenediamine, said ketone containing not more than 8 parts per million of dissolved oxygen.

6. A deterioration inhibitor for cracked gasoline comprising a solution in acetone of N,N'-diisopropyl-p-phenylenediamine, said acetone containing not more than 8 parts per million of dissolved oxygen.

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