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PETROLEUM DISTILLATE PRODUCTS

Louis A. Clarke, Fishkill, and Harry Levin, Beacon, N. Y., assignors to The Texas Company, New York, N. Y., a corporation of Delaware

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This invention relates to petroleum distillate products, such as gasoline and kerosene, and has to do particularly with petroleum distillate fuels of the class of cracked gasolines, which normally tend to deteriorate with respect to anti-knock and color and to form gum on storage, and to the provision of antioxidants or gum inhibitors in such products in sufficient quantity to substantially retard the deterioration and gum formation.

Petroleum distillate fuels, as commercially produced, often contain unstable unsaturated hydrocarbons which deteriorate on storage. Cracked gasolines produced by modern cracking processes, especially vapor phase cracking, are particularly sensitive to light and oxygen, and under conditions of handling or storage chemical changes take place which affect the color, increase the gum formation, and reduce the anti-knock properties. These changes may occur independently, simultaneously or in pairs. Although the chemistry of these changes is not thoroughly understood, it is quite generally known that certain stabilizing or inhibiting agents substantially prevent such undesirable changes from occurring.

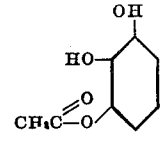
The present invention has for its object the provision of a new and improved inhibitor which will effectively retard or prevent undesirable changes from taking place in commercial gasolines and the like on storage or handling.

The formation of color in gasolines is particularly undesirable since there is imparted to the oil an undesirable appearance characteristic of unrefined products. Changes in color of gasoline are usually an indication of the formation of gums, polymers or other impurities which not only form deposits on dispensing equipment, but also may impair the operation of internal combustion engines, such as clogging of the gasoline feed lines and sticking of the valves in the motor. In certain types of discoloration and often in the initial stages thereof, it is possible by suitable treatment with antioxidants to bleach the gasoline whereby its initial color is substantially restored.

The anti-knock property of a gasoline is often due to the cracked constituents therein and the higher anti-knock fuels are often quite unstable due to the presence of hydrocarbons from cracking. The loss of anti-knock property of gasolines on storage not only makes marketing difficult due to the uncertainty of the anti-knock value of the product, but also causes considerable economic loss in order to restore such gasolines to their original anti-knock value.

We have now discovered that unstable gasolines may be stabilized or the deterioration substantially retarded or, in case substantial deterioration has taken place, material restoration of the original properties may be achieved, by treating the fuel with the new and improved inhibiting or stabilizing agents which are the subject of the present invention. These inhibitors are effective, when added to fresh gasolines, normally tending to deteriorate on storage, in preventing deterioration such as loss of color and anti-knock properties, and in retarding gum formation. The reagents are also often effective in reversing changes which have taken place on storage when such deteriorated gasolines are treated with the reagents.

The compounds which we have found to be valuable for use, according to the present invention, are the esters of the polyhydric phenols or polyhydroxy benzenes, such as pyrogallol monoacetate, having the following structural formula:



Pyrogallol monoacetate

The esters of the polyhydric phenols may be prepared according to methods described in the literature, to which reference may be made, particularly Beilstein, Vol. VI, p. 1082 (1923 edition) and Freidlander, Vol. VI, pp. 1118 and 1119. In general, the compounds may be prepared by reacting the polyhydric phenol with the fatty acid or fatty acid anhydride in the presence of a small amount of sulfuric acid. The type of ester obtained usually depends on the proportions of phenol and acid employed. By using proper molecular proportions the ester desired may ordinarily be obtained. A more convenient method may be to prepare the higher ester and then heat it with the proper amount of the phenol to yield the lower ester. We prefer, in general, to use the mono esters or other esters containing at least one free hydroxyl group. In the case of pyrogallol monoester, it is possible to treat one mol of pyrogallol with three mols of acid and thereby obtain the triester. The latter is then heated with two mols of pyrogallol to produce the monoester.

The polyhydric phenols which may be used as starting materials to form the esters thereof comprise the isomeric di- and trihydric phenols. In-

cluded within these classes are the three isomeric dihydroxy benzenes, pyrocatechol, resorcinol and hydroquinone and the three isomeric trihydroxy benzenes, pyrogallol, phloroglucinol and 1,2,4-trihydroxy benzene.

The fatty acids which have been found useful in the preparation of the esters may be either the saturated or unsaturated lower or higher fatty acids, the aromatic carboxylic acids or the alkyl or aryl substituted derivatives thereof. The lower fatty acids intended to be included are acetic, acrylic, propionic, butyric, isobutyric, crotonic, isocrotonic, valeric, allyl acetic, caproic, heptoic, caprylic and capric acids. Among those of the higher fatty acid series may be mentioned lauric, myristic, oleic, stearic, and palmitic. The aromatic carboxylic acids which are suitable for use include benzoic, phenylacetic, o-, m- and p-toluic, hydrocinnamic, o-, m- and p-tolylacetic and o-, m-, and p-ethylbenzoic. The complex acids that are produced by the oxidation of paraffin wax may also be used to advantage.

The quantity of inhibitor necessary to be used to obtain the desired results may vary somewhat but from an economical standpoint or because of limited solubility small amounts are used and it has been found that only minute amounts are ordinarily sufficient to be effective. In general, quantities varying between about 0.005% and 0.025% by weight are satisfactory, and we prefer to use around 0.01%. By suitable control tests it is possible to determine the minimum quantity that will give the proper stability to the fuel.

The inhibitor may be dissolved directly in the oil to be treated but we have found it advantageous in certain instances to prepare a solution of the inhibitor in a solvent, preferably a mutual solvent for both the inhibitor and the oil. Solvents such as acetone, benzol, or mixtures thereof are suitable. The solution of the inhibitor in the solvent is then dispersed in the oil.

A suitable method for testing the stability of oils or the effectiveness of inhibitors is the accelerated oxidation test as described by Hunn, Fischer and Blackwood in the Journal of the Society of Automotive Engineers, vol. 26, page 34, (1930). In accordance with this test the gasoline is placed in a bomb under 100 lbs. per sq. in. oxygen pressure at 212° F. and the induction period measured. The induction period is that time which elapses before active oxidation occurs in the accelerated oxidation test and is indicated by a fall in pressure of the oxygen in the bomb.

In practicing the present invention a sample of cracked gasoline which had an induction period of 138 minutes was treated by incorporating therein 0.01% of pyrogallol monoacetate. The induction period on the treated sample was 1710 minutes. Substantially similar results may also be obtained with pyrogallol monostearate or pyrogallol monobenzoate.

Obviously many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. The method of stabilizing cracked gasolines against deterioration and gum formation, which comprises adding to the gasoline a small amount of an inhibitor consisting of a polyhydric phenol esterified with a carboxylic acid selected from the group consisting of lower fatty acids and higher fatty acids of the class of oleic, stearic and palmitic, and benzoic acid.

2. A cracked gasoline normally tending to deteriorate and form gum on storage and containing a small amount of an inhibitor consisting of a polyhydric phenol esterified with a carboxylic acid selected from the group consisting of lower fatty acids and higher fatty acids of the class of oleic, stearic and palmitic, and benzoic acid, to stabilize said gasoline.

3. The method of stabilizing cracked gasolines against deterioration and gum formation which comprises incorporating in the gasoline a small amount of an inhibitor consisting of a polyhydric phenol esterified with a carboxylic acid selected from the group consisting of lower fatty acids, stearic and benzoic acids.

4. A cracked gasoline normally tending to deteriorate and form gum on storage and containing, in sufficient amount to stabilize the gasoline, a polyhydric phenol esterified with a carboxylic acid selected from the group of lower fatty acids, stearic and benzoic acids.

5. The method of stabilizing cracked gasolines against deterioration and gum formation which comprises incorporating in the gasoline a small amount of an inhibitor consisting of pyrogallol esterified with a carboxylic acid selected from the group consisting of lower fatty acids, stearic and benzoic acids.

6. A cracked gasoline normally tending to deteriorate and form gum on storage and containing, in sufficient amount to stabilize the gasoline, pyrogallol esterified with a carboxylic acid selected from the group consisting of lower fatty acids, stearic and benzoic acids.

7. The method of treating petroleum distillates of the class of gasoline and kerosene, normally tending to deteriorate with respect to color and gum in light and on storage, which comprises adding to the distillate a small amount of a low molecular weight fatty acid ester of a polyhydric phenol whereby such deterioration is substantially retarded.

8. A composition of matter comprising a petroleum distillate fuel of the class of gasoline and kerosene unstable with respect to color and gum in light and on storage, and containing a low molecular weight fatty acid ester of a polyhydroxy benzene in sufficient amount to substantially stabilize said fuel.

9. The method of treating motor fuels of the class of gasoline and kerosene, normally tending to deteriorate with respect to color and gum in light and on storage, which comprises incorporating in the fuel a small amount of a monoacetic acid ester of a polyhydric phenol to retard such deterioration, said monoacetic acid ester resulting from the esterification of an hydroxyl radical of the polyhydric phenol by an acetyl group.

10. A cracked gasoline normally tending to deteriorate and form gum on storage and containing a monoacetic acid ester of a polyhydric phenol, in sufficient amount to retard such deterioration and gum formation.

11. The method of improving the character of motor fuels of the class of gasoline and kerosene, normally tending to deteriorate with respect to color and gum in light and on storage, which comprises adding to the fuel a small amount of a monostearic acid ester of a polyhydric phenol to retard such deterioration, said monostearic acid ester consisting of the esterification product of an hydroxyl radical of the polyhydric phenol and a stearyl group.

12. A cracked gasoline normally tending to deteriorate and form gum on storage and containing a monostearic acid ester of a polyhydric phenol in sufficient amount to retard such deterioration and gum formation.

13. The method of treating motor fuels of the class of gasoline and kerosene, normally tending to deteriorate with respect to color and gum in light and on storage, which comprises adding to the fuel a monobenzoic acid ester of a polyhydric phenol in sufficient amount to retard such deterioration, said monobenzoic acid ester containing a benzoyl radical substituted for a hydrogen of one of the hydroxyl groups of the polyhydric phenol.

14. A cracked gasoline normally tending to deteriorate and form gum on storage and containing a monobenzoic acid ester of a polyhydric phenol in sufficient amount to retard such deterioration and gum formation.

15. The method of treating cracked gasolines and the like to retard deterioration with respect to color and gum in light and on storage, which comprises adding to the gasoline a small amount of pyrogallol monoacetate.

16. A cracked gasoline normally unstable with respect to color and gum in light and on storage, and containing a small amount of pyrogallol monoacetate to stabilize said gasoline.

17. The method of inhibiting gum formation in cracked gasoline, which comprises adding to the gasoline a small amount of pyrogallol monostearate.

18. A cracked gasoline normally unstable with respect to color and gum in light and on storage, and containing a small amount of pyrogallol monostearate to stabilize said gasoline.

19. The method of inhibiting gum formation in cracked gasoline, which comprises adding to the gasoline a small amount of pyrogallol monobenzoate.

20. A cracked gasoline normally unstable with respect to color and gum in light and on storage, and containing a small amount of pyrogallol monobenzoate to stabilize said gasoline.

LOUIS A. CLARKE.
HARRY LEVIN.