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UNITED STATES PATENT OFFICE

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GUM INHIBITOR

No Drawing. Application filed March 25, 1930. Serial No. 438,896.

This invention relates to improvement in means for the protection of liquid hydrocarbon products against the formation of insoluble and gummy products, and more particularly to improved materials for use with unsaturated liquid hydrocarbons which may be used as fuels. The improved materials contemplated may protect the liquid hydrocarbons against discoloration.

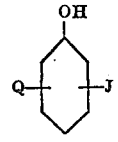
Liquid hydrocarbons as commercially produced, particularly when prepared by the distillation or cracking of petroleum, possess a tendency to discolor on standing and to form gums and resinous substances. Gasolines produced by the modern cracking processes are extremely complicated mixtures comprising many constituents, the character of these constituents and the relative proportions of different constituents depending upon the source of the crude and the particular cracking process employed. Besides the normal and branched chain paraffines, there are often present substantial percentages of aromatic hydrocarbons. The crude cracked gasoline also always contains unsaturated hydrocarbons, such for example as olefines and diolefines. Although there may be present some compounds containing a triple bond, these are probably not compounds such as may be formed by the polymerization of acetylene, but rather such compounds as may be formed by the isomerization of dienes and having the general formula C_nH_m where m is greater than n, but less than $2n+2$. In certain instances unsaturated compounds are intentionally added to gasolines. The gasolines resulting from such additions may or may not have contained unsaturated hydrocarbons before the addition was made. These unsaturated compounds, regardless of how they were incorporated in the gasoline, in the presence of air are capable of oxidation to form a series of products, some of which are resinous or gummy. The diolefines, and more unsaturated hydrocarbons, are particularly easily oxidized. Differences in structure other than the degree of unsaturation cause considerable variation in the tendency to oxidize, but in general the ease of oxidation increases with the degree of unsaturation. The more recent pressure methods of vapor phase cracking result in a considerably higher percentage of diolefines than the older methods, and it has been stated that these products may run as high as 8 to 15% in unrefined gasoline.

It has been necessary to treat the crude products resulting from the more recent cracking processes in some manner to remove the greater part of these more highly unsaturated products. Among these methods of treatment may be mentioned the sulfuric acid treatment and the fuller's earth vapor phase treatment. While these methods of purification may remove the greater part of the highly unsaturated compounds, it is found that many brands of gasoline tend to discolor on storage and to form a certain amount of gum. The gum appears to be a complex mixture of polymerized hydrocarbons, resins, acids, aldehydes, ketones and peroxides. Its formation is distinctly detrimental in all cases. For example, the deposition of gum in gasoline gives a sticky substance which deposits upon the walls and bottom of the container, and which may cause serious trouble if formed or deposited in the fuel system of internal combustion engines. The soluble portion of the gum is also objectionable because of the introduction of a non-volatile component into the gasoline.

This invention has for an object the inhibition of the formation of these insoluble gums and resins, with an attendant improvement in the quality of the hydrocarbon and freedom from the difficulties introduced by the formation of the more or less insoluble and sticky, gummy material, such as irregular flow in the fuel system of internal combustion engines. A further object is to make

t possible to use as an internal combustion uel, liquid hydrocarbons such as gasoline, hat contain larger amounts of highly unaturated compounds than commercially used it present. A product of this sort can e produced at a lower cost, and possesses n certain cases, improved anti-knock proprties. Other objects will appear hereinafter.

These objects are accomplished by the present invention wherein hydroxy-benzene compounds are added to gasoline or oils having similar characteristics. The incorporation may be made at any suitable stage of the production of the substance to be preserved. The invention includes compounds of the general formula $R-(OH)_n$, where R represents a benzene nucleus which may or may not be substituted and n is an integer equal to or greater than 1. More specifically the general formula of the compound used is:



J being a member of the group hydrogen, hydroxyl, alkyl and alkoxy and Q being a member of the group hydrogen, hydroxyl, alkyl, alkoxy, and hydrocarbon radicals other than alkyls.

The invention will be readily understood from a consideration of the examples which follow. In these examples the copper dish test has been used. This is a common method of testing gum formation in gasoline and consists in evaporating a 100 cc. sample of the hydrocarbon from a weighed copper dish on a steam bath and determining the weight of the gum residue. This gum residue is taken as an indication of the stability of the hydrocarbon with respect to gum formation.

Example 1

When 0.014 gm. pyrogallol was added to 100 cc. of gasoline containing unsaturated hydrocarbons and the gasoline subjected to the copper dish test the amount of gum formed was 6 mg. An equal portion of the same gasoline containing no stabilizer tested in the same way at the same time gave 53 mg. gum.

Example 2

Another experiment similar to Example 1 was carried out using resorcinol. The unstabilized control sample gasoline gave 53 mg. gum/100 cc. Only 27 mg. gum/100 cc. were obtained from a sample of the same gasoline containing 0.014 gm. resorcinol.

Example 3

Thymol was added to the extent of 0.03 gm. per 100 cc. to a freshly distilled cracked gasoline and a 100 cc. portion of the treated gasoline subjected to the copper dish test. The amount of gum formed in the presence of the thymol was 196 mg. whereas from an unstabilized sample of the same gasoline tested at the same time 276 mg. gum per 100 cc. were obtained.

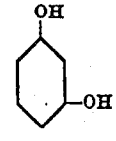
In the general class of hydroxy-benzenes certain subclasses and certain specific compounds along with those mentioned in the above examples merit special mention. For instance, use may be made of:

(1) The di-hydroxy-benzenes

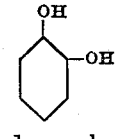
Hydroquinone



Resorcinol

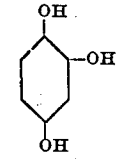


Catechol

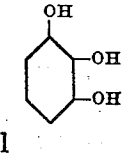


or (2) the tri-hydroxy-benzenes

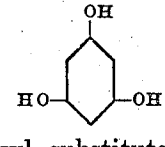
Hydroxy-quinol



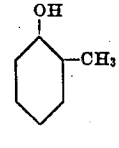
Pyrogallol

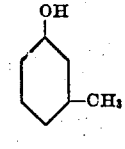


Phloroglucinol



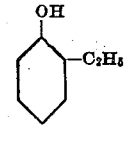
or (3) the alkyl substituted hydroxy-benzenes, for example, (3*a*) the cresols

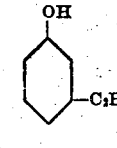






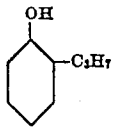
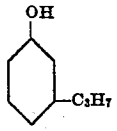
(3*b*) the ethyl-phenols



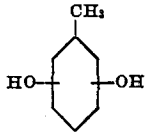




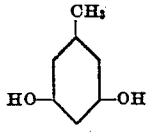
(3*c*) the propyl-phenols


(3*d*) the di-hydroxy-toluenes

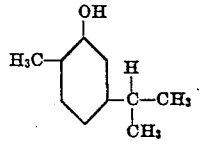


Orcinol

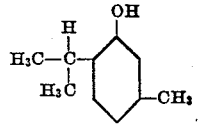


(4) Substituted hydroxy-benzenes are suitable, for example, use may be made of:

Carvacrol

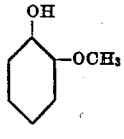


Thymol

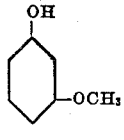


(5) Use may also be made of alkoxy-hydroxy-benzenes as:

Guaiacol



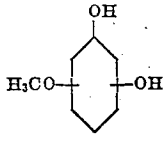
Resorcinol-mono-methyl-ether



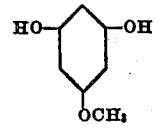
Hydroquinone-mono-methyl-ether



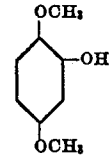
Methoxy-di-hydroxy-benzenes



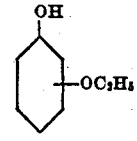
Phloroglucinol-mono-methyl-ether



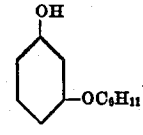
1:4-di-methoxy-2-hydroxy-benzene



Mono-ethoxy-hydroxy-benzenes

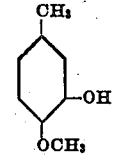


Resorcinol-mono-hexyl-ether (hexyl-resorcinol)

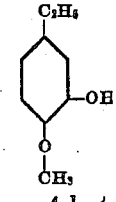


(6) Suitable for use also are the alkyl-alkoxy-hydroxy-benzenes, for example:

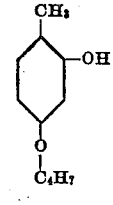
Creosole



1-ethyl-3-hydroxy-4-methoxy-benzene

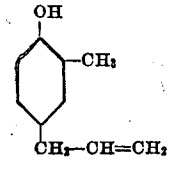


1-methyl-2-hydroxy-4-butoxy-benzene



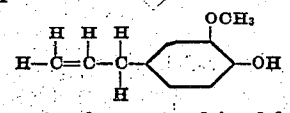
(7) The alkyl-hydroxy-benzenes may be substituted by other than alkoxy groups, for example:

1-hydroxy-2-methyl-4 (3-propenyl)-benzene

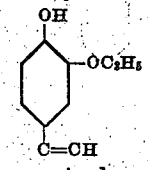


(8) The alkoxy-hydroxy-benzenes may be substituted with groups other than alkyls for instance:

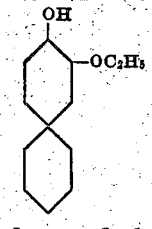
Eugenol



1-hydroxy-2-ethoxy-4-ethinyl-benzene



1-hydroxy-2-ethoxy-4-phenyl-benzene



It is to be understood that other isomers and homologues in the classes mentioned above may be used. In certain cases it may be advantageous to use mixtures of two or more of the compounds covered by this invention. It will be appreciated that the examples outlined above and specific compounds mentioned are given merely for the purpose of illustrating the invention and that it is not intended that the invention should be limited to the specific inhibitors named. The concentration of the gum inhibiting agent may vary to secure protection against gumming to a greater or less degree depending upon the nature of the hydrocarbon fuel, the particular inhibitor or inhibitors used, the actual concentration of the inhibitor, the conditions of storage and time of protection desired. Ordinarily the amount of inhibitor incorporated in the gasoline ranges from 0.001 to 0.1% by weight. It will be apparent, however, that this range is not given as limiting since lesser or greater amounts may be used in specific instances within the scope of this invention. In most instances no marked advantage is gained by using more than the maximum amount set out above, but in any event the range given appears to be sufficient for the grades of gasoline now on the market. While good results have been obtained with the specific inhibitors given above in the examples, the particular compound preferred is pyrogallol.

The materials used herein seem by virtue of their anti-oxidizing properties to inhibit and check the formation of organic peroxides which catalyze gum formation. By checking this catalysis, it is possible to inhibit a large portion of the undesirable gum.

Obviously this invention is of great importance in freeing internal combustion engines from the annoyance and improper functioning due to the deposition of gum in the fuel containers or fuel systems.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that we do not limit ourselves to the specific embodiments thereof except as defined in the appended claims.

We claim:

1. Gasoline otherwise capable of gumming and containing 0.001 to 0.1% of creosole.

2. Gasoline produced by the cracking of petroleum oils and containing a small amount of creosole as a gum inhibitor.

3. Gasoline comprising a substantial quantity of unsaturated hydrocarbons and containing a small amount of creosole as a gum inhibitor.

4. Gasoline comprising a diene and containing a small amount of creosole as a gum inhibitor.

5. A composition of matter comprising a hydrocarbon fuel and a small amount of creosole as a gum inhibitor.

6. A composition of matter comprising a liquid hydrocarbon fuel for internal combustion engines and a small amount of creosole as a gum inhibitor.

7. A liquid hydrocarbon product comprising a hydrocarbon of the formula C_nH_m, wherein m is greater than n but less than $2n+2$, and containing a small amount of creosole as a gum inhibitor.

8. The process comprising adding a small amount of creosole to gasoline capable of forming a gum upon exposure to air and/or oxygen and/or light and/or heat.

9. In the process of inhibiting the formation of gum in a gasoline comprising substances adapted to form a gum in the presence of oxygen and/or light and/or heat and/or air, the step of adding thereto creosole.

10. The process of inhibiting gum formation in liquid hydrocarbons comprising adding thereto creosole.

11. The process of restraining gum formation in gasoline adapted to gum comprising treating the gasoline with 0.001 to 0.1% of creosole.

12. A hydrocarbon motor fuel comprising constituents adapted to form gums and/or resinous substances upon exposure to oxygen and having incorporated therein about 0.001 to 0.1% of creosole.

In testimony whereof we affix our signatures.

WILLIAM S. CALCOTT.
IRA E. LEE.

Certificate of Correction

Patent No. 1,884,559. October 25, 1932.

WILLIAM S. CALCOTT ET AL.

It is hereby certified that error appears in the printed specification of the above-numbered patent requiring correction as follows: Page 4, line 15, for " C=CH " read C≡CH; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 10th day of January, A. D. 1933.

[SEAL.]

M. J. MOORE,
Acting Commissioner of Patents.