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GUM INHIBITOR FOR HYDROCARBONS

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10 Claims. (Cl. 44—9)

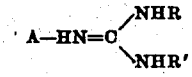
This invention relates to improvement in means for the protection of liquid hydrocarbon products against discoloration and formation of insoluble and gummy products, and more particularly to improved materials for use with unsaturated liquid hydrocarbons which may be used as fuels.

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 $2n+2$. These unsaturated compounds 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.

Our 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 and lubricating systems of internal combustion engines. A further object is to make it possible to use as an internal combustion fuel, liquid hydrocarbons such as gasoline, that contain larger amounts of highly unsaturated compounds than commercially used at present. A product of this sort can be produced at a lower cost, and possesses in certain cases, improved anti-knock properties.

We have found that by treating hydrocarbons, and specifically unsaturated hydrocarbons such as hydrocarbon fuels, and more specifically such as cracked gasoline or gasoline which has a tendency to form gum, the gum formation can be very appreciably inhibited if the hydrocarbon is treated with a diaryl guanidine salt of a fatty acid. More specifically, our invention relates to the use as gum inhibitors for hydrocarbons of compounds of the type



in which A is a fatty acid and in which R is an aryl group, and R′ is an aryl group which may be the same as or different from R, and in which both R and R′ may contain alkyl substituents. By way of illustrating our invention, we may set forth the following examples:

Example 1

Diorthotolylguanidine-stearate was dissolved to the extent of 0.002% in an unstable gasoline which, when untreated, developed considerable yellow color within from six to eight hours, and after three weeks time contained a large amount of insoluble gum and resin when placed in a glass bottle and exposed to sunlight. The identical

sunlight exposure test was made with a sample treated with diorthotolylguanidine-stearate, and it was observed that a sample remained essentially colorless and contained no gum residues after three weeks exposure to sunlight.

Example 2

During a sunlight exposure test, using glass bottles, a gasoline sample treated with 0.002% diphenylguanidine butyrate, the product obtained by mixing 1 mol of diphenylguanidine and 1 mol of butyric acid, remained colorless and free from insoluble gums for three weeks time, whereas yellowing and gum formation occurred to a very marked extent in a check sample of the same gasoline containing no gum inhibitor. The diphenylguanidine butyrate obviously gave protection against discoloration and gum formation.

Throughout our specification by fatty acid we mean mono-carboxylic acid derivatives of an aliphatic hydrocarbon such as, for example, propionic, palmitic, acetic, butyric, stearic, oleic acids, and the like. Within the contemplation of our invention will be found salts formed by combining such fatty acids with diaryl guanidines such as, for example, diparatolyl guanidine, dixylyl guanidine, phenyl tolyl guanidine, di-alpha-naphthyl guanidine, diortho anisyl guanidine, as well as diorthotolyl guanidine and diphenyl guanidine.

In some cases it has been found advisable to use the acid salt of a mixture of guanidines rather than a single pure product. Conversely, a single guanidine or one or more guanidines may be combined with a mixture of fatty acids falling within the class described above. The formation of the fatty acid salt of the guanidines may be made, for example, by a process similar to that described in U. S. Patent 1,747,187 to Winfield Scott. It has been found, in some cases, that a combination of two different guanidine salts is superior in its effect on gasoline to either guanidine salt used singly. In general, however, we prefer to use the fatty acid salt of diorthotolyl guanidine and specifically the stearic acid salt of ditolyl guanidine, which is the product formed by fusing 1 mol of stearic acid with 1 mol of diorthotolyl guanidine. We may use higher or lower concentrations of any members of the class of compounds represented by the general formula given hereabove to secure marked inhibition of gum formation, although, of course, the degree of inhibition will vary depending upon the individual guanidine salt, the concentration of guanidine salt employed, and the nature of the hydrocarbon fuel. In general, the concentration of inhibitor may vary from 0.00025 of 1% to .01 of 1% or higher, depending upon the nature of the gasoline, the storage conditions, the length of time protection is desired, and the specific inhibitor being used. It will be obvious, of course, that these percentages may be varied within wide limits.

Clearly, our 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 system and explosion chamber. However, it is to be understood that our invention is not limited to the gum inhibition in gasoline fuels. Other hydrocarbon fuels and other hydrocarbons may be effectively treated with our class of gum inhibitors. Thus, transformer oils, lubricating oils and unsaturated hydrocarbons containing olefines and diolefines are susceptible to treatment.

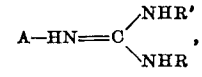
As many apparently widely different embodiments of this invention may be made without departing from the spirit thereof, it is to be understood that we do not limit ourselves to the foregoing examples or descriptions except as indicated in the following patent claims.

We claim:

1. Gasoline normally tending to form gum, to which has been added, in sufficient amount to inhibit the formation of gum, a diaryl guanidine salt of a fatty acid.

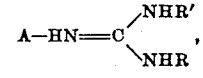
2. Gasoline normally tending to form gum, to which has been added, in sufficient amount to inhibit the formation of gum, a diaryl guanidine salt of a fatty acid from the group comprising acetic, butyric, propionic, palmitic, stearic and oleic acids.

3. Gasoline normally tending to form gum, to which has been added, in sufficient amount to inhibit the formation of gum, a compound of the type



in which A represents a fatty acid, and R an aryl nucleus, and R' an aryl nucleus which may be, although not necessarily is, the same as R and in which, as in R, there may be alkyl substituents.

4. Gasoline normally tending to form gum, to which has been added, in sufficient amount to inhibit the formation of gum, a compound of the type



in which A is a fatty acid from the class comprising acetic, butyric, propionic, palmitic, stearic and oleic acids, and R an aryl nucleus, and R' an aryl nucleus which may be, although not necessarily is, the same as R and in which, as in R, there may be alkyl substituents.

5. Gasoline normally tending to form gum, to which has been added, in sufficient amount to inhibit the formation of gum, a diorthotolyl guanidine salt of a fatty acid.

6. Gasoline normally tending to form gum, to which has been added, in sufficient amount to inhibit the formation of gum, a diorthotolyl guanidine salt of a fatty acid from the class comprising acetic, butyric, propionic, palmitic, stearic and oleic acids.

7. Gasoline normally tending to form gum, to which has been added, in sufficient amount to inhibit the formation of gum, the diorthotolyl guanidine salt of stearic acid.

8. Gasoline normally tending to form gum, to which has been added, in sufficient amount to inhibit the formation of gum, a diphenyl guanidine salt of a fatty acid.

9. Gasoline normally tending to form gum, to which has been added, in sufficient amount to inhibit the formation of gum, a diaryl guanidine salt of butyric acid.

10. Gasoline normally tending to form gum, to which has been added, in sufficient amount to inhibit the formation of gum, the diphenyl guanidine salt of butyric acid.

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