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GUM INHIBITOR FOR GASOLINE

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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 $C_n H_m$ 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. 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 color and gum, with an attendant imrovement in the quality of the hydrocarbon fuel. 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 liquid hydrocarbons, such as cracked gasoline or gasoline which has a tendency to become discolored and form gum, with certain organic compounds the color formation can be very appreciably inhibited.

By way of example, if 0.05% of diethanolamine is dissolved in unrefined cracked gasoline, the formation of gum otherwise noticeable in the gasoline is very appreciably inhibited. By way of a laboratory test, the common method of measuring gum formation in a given gasoline is to evaporate 100 cc. of the fuel in a copper dish in a steam bath, and to determine the gum residue by the increase in the weight of the dish. When subjected to such a test the gasoline referred to in the example above gave the following results: A control sample of gasoline containing no added agent produced 86 mgm. of gum per 100 cc., whereas a 100 cc. sample of the same gasoline containing 0.05% of diethanolamine formed only 33 mgm. of gum per 100 cc. sample. The decrease in gum formation, because of the presence of the amine, was 53 mgm. or 62%.

If to a gasoline which undergoes rapid discoloration and gives rise to gum formation upon exposure to direct sunlight .002% of dibutylamine be added, the aging qualities of the gasoline will be substantially improved. In an aging

test wherein the gasoline was permitted to stand exposed to sunlight an untreated sample of gasoline became yellow in about five hours, and the formation of insoluble gum was evidenced in about five days. A sample of the same gasoline treated with dibutylamine, on the other hand, remained colorless, clear and free from gum over a three weeks' test period of constant exposure to light.

It will be understood that the examples given above have been made merely for the purpose of illustrating our invention, and that we do not wish to be restricted to the specific amines, amounts of inhibitor or types of hydrocarbons set forth in the example. We have tested many of these compounds over prolonged periods and found them to be effective in the prevention of gum and color formation even when the hydrocarbon has been exposed to direct sunlight. Following are some of the substances which we have found to be effective inhibitors: Alpha-methyl-hydroxylamine, allylamine, N-amylamine, sec. butylamine, di-iso-butylamine, N-dibutylamine, diethanolamine, iso-amylamine, iso-butylamine, diallylamine, di-iso-amylamine, butylamine, triethanolamine.

In some cases it has been found advisable to use a mixture of aliphatic amines rather than a single pure product. It has been found in some cases that a combination of two different amines is superior in its effect in gasoline to either amine used singly. In other cases we may, as a matter of economy, use a mixture of amines such, for example, as those that may be obtained by the aminization of mixed amyl chlorides.

We may use higher or lower concentrations of any members of the class of compounds represented by the examples given hereabove and secure inhibition of gum and color formation, although, of course, the degree of gum inhibition will vary depending upon the individual amine, the concentration of amine employed, and the nature of the hydrocarbon.

We have found that gasoline which otherwise is seriously discolored by sunlight with the attendant formation of large quantities of gums, when treated with certain aliphatic amines may be exposed to sunlight over a long period of time with but little, if any, color formation resulting.

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. A cracked gasoline normally unstable with respect to color and gum formation and containing, as a color and gum formation inhibitor, a small proportion of an aliphatic amine selected from the group consisting of a polybutyl amine and an amylamine.

2. A motor fuel comprising cracked gasoline which normally tends to become discolored and a small proportion of an aliphatic polybutyl amine.

3. A cracked gasoline normally unstable with respect to color formation and containing, as a color formation inhibitor a small proportion of an aliphatic dibutyl amine.

4. A cracked gasoline normally unstable with respect to color formation and containing, as a color formation inhibitor, a small proportion of an aliphatic amylamine.

5. A cracked gasoline normally unstable with respect to color formation and containing, as a color formation inhibitor, a small proportion of an aliphatic amine having at least two amyl groups.

6. A motor fuel comprising cracked gasoline normally unstable with respect to color formation and containing as a color formation inhibitor a small proportion of a mixture of aliphatic butylamines.

7. A motor fuel comprising cracked gasoline normally unstable with respect to color formation and containing, as a color formation inhibitor, a small proportion of an aliphatic diamylamine.

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