

UNITED STATES PATENT OFFICE

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GUM INHIBITOR FOR HYDROCARBONS

No Drawing.

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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_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 caused 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 liquid hydrocarbons, such as lubricating oils, transformer oils and hydrocarbon fuels, such as cracked gasoline or gasoline which has a tendency to form gum, with certain organic compounds the gum formation can be very appreciably inhibited. More specifically, our

invention relates to the use as gum inhibitors of compounds of the type represented by:



in which R is an aryl group which may contain alkyl substituents or alkoxy substituents, and in which R' may be an alkyl group, an aryl group, or an aralkyl group.

By way of illustrating our invention, if to a gasoline which undergoes rapid discoloration and gives rise to gum formation upon exposure to direct sunlight, .05% of acetanilide 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 acetanilide remained colorless, clear and free from gum over a long test period of constant exposure to light, and showed no appreciable formation of color and very little formation of gum at the end of a year. It will be understood that the example given above has been described merely for the purpose of illustrating our invention, and that we do not wish to be restricted to the specific amine, amount of inhibitor or type of hydrocarbon set forth in the example.

We have discovered that compounds produced by the acetylation or, in general, acylation of aromatic amines and specifically primary aromatic amines are decidedly effective in preventing the formation of gum and color in hydrocarbons. We have tested many of these compounds over prolonged periods, and found them to be effective in the prevention of gum formation under conditions which normally give rise to the formation of large quantities of gum. In addition to acetanilide, acetyl-p-toluidine and acetyl-o-toluidine are effective. Moreover, such compounds as benz-anilide and benzyl-p-toluidine are useful. This property of preventing gum formation is not limited to the acetyl compounds, but is possessed also by the products obtained by the action of other aliphatic acids on aromatic amines. Propion-anilide, for example, is very effective. Compounds formed by the action of these acids on the naphthyl amines are also effective. An example of this class is acet-a-naphthylamine. As stated above, the aryl group in the general formula may contain alkyl or alkoxy substituents. Acet-p-phenetidine is effective. In some cases it has been found advisable to use a mixture of the substances comprising our invention 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 upon hydrocarbons to either amine used singly. In other cases we may, as a matter of economy, use a mixture of amines.

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

In general, we have found that acyl derivatives of aromatic amines including derivatives containing alkyl and alkoxy substituents are effective gum inhibitors when added to liquid hydrocarbons such as cracked gasoline, kerosene, transformer oils, lubricating oils, dienes and similar unsaturated compounds. We have found that, for example, gasoline which otherwise is seriously discolored by sunlight with the attendant formation of large quantities of gums when treated with an acyl derivative and aromatic amine may be exposed to sunlight over a long period of time with but little, if any, gum formation resulting. Obviously, our invention is of great importance in freeing internal combustion engines from the annoyance and improper functioning due to the deposit in the fuel and lubricating systems.

It will be understood throughout the specification and appended claims that where R is used to denote aryl radicals we intend to include in the class described alkyl and alkoxy substituents.

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 composition of matter comprising a petroleum distillate fuel containing an acyl derivative of an aromatic amine.

2. Gasoline containing a small amount of an acyl derivative of an aromatic amine.

3. Gasoline produced by the cracking of petroleum oils containing as a gum inhibitor a small amount of an acyl derivative of an aromatic amine.

4. A composition of matter comprising a petroleum distillate fuel containing a substance of the type $\text{R}-\text{NH}-\text{CO}-\text{R}'$, in which R is a substance from the group comprising aryl radicals, alkyl substituents and alkoxy substituents of aryl groups, and R' is a substituent from the group comprising alkyl radicals and aryl radicals.

5. Gasoline containing a small amount of a substance of the type $\text{R}-\text{NH}-\text{CO}-\text{R}'$, in which R is a substance from the group comprising aryl radicals, alkyl substituents and alkoxy substituents of aryl groups and R' is a substance from the group comprising alkyl radicals and aryl radicals.

6. Gasoline produced by the cracking of petroleum oils containing, as a gum inhibitor, a small amount of a substance of the type $R-NH-CO-R'$, in which R is a substance from the group comprising aryl radicals, alkyl substituents and alkoxy substituents of aryl groups, and R' is a substance from the group comprising alkyl radicals and aryl radicals.

7. A petroleum distillate fuel containing in appreciable amounts and as an impurity a hydrocarbon of the formula C_n-H_m wherein m is greater than n but less than $2n+2$, together with an acyl derivative of an aromatic amine.

8. A petroleum distillate fuel containing in appreciable amounts and as an impurity a hydrocarbon of the formula C_n-H_m wherein m is greater than n but less than $2n+2$, together with a substance of the type $R-NH-CO-R'$ in which R is a substance from the group comprising aryl radicals, alkyl substituents and alkoxy substituents of aryl groups, and R' is a substance from the group comprising alkyl radicals and aryl radicals.

9. A petroleum distillate fuel containing in appreciable amounts and as an impurity a hydrocarbon of the formula C_n-H_m wherein m is greater than n but less than $2n+2$, together with acetanilide.

10. A petroleum distillate fuel containing in appreciable amounts and as an impurity a diene, together with an acyl derivative of an aromatic amine.

11. A petroleum distillate fuel containing in appreciable amounts and as an impurity a diene, together with a substance of the type $R-NH-CO-R'$, in which R is a substance from the group comprising aryl radicals, alkyl substituents and alkoxy substituents of aryl groups, and R' is a substance from the group comprising alkyl radicals and aryl radicals.

12. A petroleum distillate fuel containing in appreciable amounts and as an impurity a diene, together with acetanilide.

13. A composition of matter comprising a petroleum distillate fuel containing acetanilide.

14. Gasoline containing a small amount of acetanilide.

15. Gasoline produced by the cracking of petroleum oils containing as a gum inhibitor a small amount of acetanilide.

In testimony whereof we affix our signatures.

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