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STABILIZATION OF MOTOR FUELS

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6 Claims. (Cl. 44—74)

This invention relates to improvements in motor fuels, specifically those such as gasoline which contains gum forming constituents. More specifically, the invention is concerned with the prevention of gum formation in motor fuels by the addition thereto of a new class of gum inhibitors; namely, N,N'-dicycloaliphatic-p-phenylenediamines.

It is a well known fact that motor fuels produced by cracking processes tend to deteriorate upon storage with the formation of undesirable gums. In general, the higher the cracking temperature employed in processing the gasoline the greater the tendency of it to form gums. Gasolines produced by the polymerization of olefins from cracking still gases and coal-tar benzole, frequently employed in motor fuels, produced by processes employing high temperatures also show gum forming tendencies. The deterioration of the motor fuel is believed to be due to unsaturated bodies in the fuel which polymerize with the formation of dark colored resinous gums thus lowering the color of the motor fuel and causing the formation of hard resinous deposits on the intake manifold and valves of the engine. It is also thought that gum formation lowers the octane rating of the fuel by removing some of the anti-knock constituents from the fuel.

The prevention of gum formation and deterioration of gasoline has been accomplished in the past by the addition of certain gum formation inhibitors such as phenols, aminophenols and various aryl and alkyl N,N' substituted p-phenylenediamines and mixtures thereof.

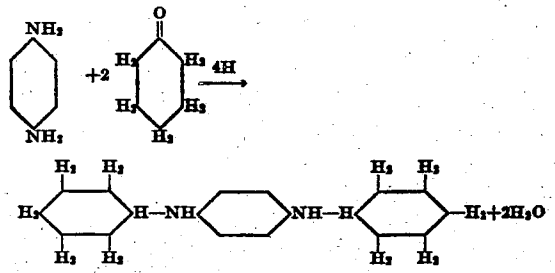
We have now discovered that N,N'-dicycloaliphatic-p-phenylenediamines, which we believe to be new compounds, may be prepared by a method to be presently described and that such compounds may be added to motor fuels, particularly cracked gasoline, thereby effectively stabilizing the fuel against deterioration and gum formation.

So far as we are aware the N,N' p-phenylenediamine gum inhibitors heretofore employed have been of such structure that the nitrogen of the p-phenylenediamine nucleus is attached to either a primary or a tertiary carbon atom. For example, the carbon atoms of phenyl groups are tertiary and are directly attached to the nitrogen atoms of the phenylenediamine nucleus in compounds such as N,N'-diphenyl-p-phenylenediamine. In the alkyl substituted p-phenylenediamines such as N,N'-butyl-p-phenylenediamine and N,N'-diisoamyl-p-phenylenediamine the nitrogen of the p-phenylenediamine nucleus is attached to a primary carbon atom. In the compounds of the present invention each nitrogen atom of the p-phenylenediamine nucleus is coupled to one secondary carbon atom of the substituent cycloaliphatic radical and it is to this distinction that we ascribe the greater effectiveness of our compounds as distinguished from those heretofore employed in gasoline as gum inhibitors.

In addition to being effective gum inhibitors the compounds of this invention possess a number of other advantages which make their use for this purpose highly desirable. The particular compounds described herein have a marked solubility in gasoline and their incorporation therein may be easily accomplished. They are, on the other hand, quite insoluble in water and since gasoline is generally stored over water they are not thereby extracted from the gasoline as frequently happens when using water soluble gum inhibitors. The compounds of the present invention are also insoluble in alkaline solutions and are not extracted from the gasoline by residual alkalies left in the gasoline after refining operations. A further and important advantage of the compounds of the present invention is that should they be oxidized by high temperatures, compounds as N,N'-diphenyl-p-phenylenediamine would be formed which are also effective as antioxidants.

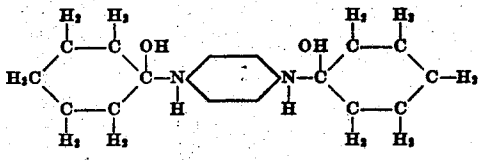
The compounds of the present invention may be prepared by mixing approximately 2 moles of a cycloaliphatic ketone with one mole of p-phenylenediamine and treating the mixture with hydrogen in the presence of a hydrogenation catalyst. The cycloaliphatic ketones which may be employed include those such as cyclohexanone; methyl cyclohexanone; dimethyl and trimethyl cyclohexanones; ethyl, propyl, butyl and amyl mono-, di- and tri-substituted cyclohexanones; cyclopentanone, methyl cyclopentanone, cycloheptanones and the like.

The reaction whereby the NN'dicycloaliphatic-p-phenylenediamines of the present invention are produced may be illustrated by the following equation, using cyclohexanone as the cycloaliphatic ketone:

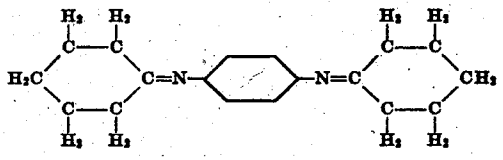


Although it has not been definitely established it would appear that during the course of this re-

action a compound of the following type is first obtained



which then splits out water to form dicyclohexylidine-p-phenylenediamine.



This latter compound is easily reduced by hydrogen to yield NN'dicyclohexyl-p-phenylene-diamine as illustrated above.

The catalytic reduction is carried out with one of the many conventional hydrogenation catalysts available such as copper chromite, Raney nickel, nickel-copper, platinum black, palladium black, nickel-alumina, nickel, copper, nickel-thoria, etc. or combinations thereof. The reduction is carried out at temperatures preferably ranging from 100 to 200° C. and at pressures within the range 500–2000 pounds per square inch. The time required may vary from 1 hour up to 10 or more hours depending upon the temperature, pressure and activity of the catalyst. In conducting this hydrogenation it is most convenient to dissolve the reactants in an inert solvent as, for example, alcohols such as isopropyl alcohol, amyl alcohol, etc., and various ethers and hydrocarbons. An excess of the ketone itself may also be employed.

The preparation of our new gum inhibitors will now be illustrated in greater detail in the following example. It will be understood, of course, that this particular example is given merely for purposes of illustration and is not intended to be in limitation of our invention since as pointed out above other cycloaliphatic ketones, hydrogenation catalysts and reaction conditions may be employed if desired.

Example

54 parts by weight of p-phenylenediamine and 196 parts by weight of cyclohexanone were dissolved in 116 parts by weight of isopropyl alcohol and 14 parts of copper chromite added thereto as catalyst. The reaction was carried out in a pressure autoclave at a temperature of 150–170° C. and a pressure varying from 1000–1670 pounds per square inch over a period of 1.5 hours. After reduction the catalyst was filtered off and the solvent removed by evaporation. NN'dicyclohexyl-p-phenylenediamine remained as a pinkish-red colored oil that crystallized on standing. The crude product thus obtained had a melting point of around 55° C. and was readily soluble in alcohols, gasoline, benzene and other common organic solvents.

The NN'-dicycloaliphatic-p-phenylenediamines prepared as described above may be used as gum inhibitors as they come directly from the hydrogenation autoclave. If desired, however, they may be further purified by distillation in vacuo.

The NN'-dicycloaliphatic-p-phenylenediamines may be employed as gum inhibitors in amounts ranging from as little as 5 parts of the inhibitor per million parts of gasoline to amounts exceeding 200 parts per million with increasingly effective results.

The NN'-dicycloaliphatic-p-phenylenediamines are effective in inhibiting gum formation in cracked gasolines, gasolines produced by polymerization of olefins, in blended gasolines containing unsaturated bodies tending to form gums and in gasolines blended with benzol, alcohols and other combustible materials. They may also be used with conventional anti-knock compositions such as tetraethyl lead fluid and with dyestuffs and other inhibitors of various kinds.

The effectiveness of our new gum inhibitors in preventing gum formation in gasoline is shown in the following table in which the results obtained with a member of our new class of compounds is given in comparison with the results obtained with n-monobutyl-p-aminophenol, a very well known and effective gasoline antioxidant, and the untreated gasoline alone. The gasoline employed was of the cracked type which had been doctor sweetened. These tests were made according to the procedure prescribed for the A. S. T. M., oxygen bomb test B 525–39T recognized in the industry as a standard method of measuring the gum forming tendencies of gasoline.

Table

A. S. T. M. oxygen bomb test B 525–39T cracked type, doctor sweetened gasoline

Inhibitor	Concentration	Induction periods, minutes
	P. P. M.	
None		36
N-monobutyl-p-aminophenol	50	121
NN'-dicyclohexyl-p-phenylenediamine	50	131

What we claim is:

1. A motor fuel containing unsaturated hydrocarbons which normally tend to develop gums, stabilized against said gum formation by the presence of a small amount of N,N'-di-cycloaliphatic-p-phenylene diamine.

2. A motor fuel containing unsaturated hydrocarbons which normally tend to develop gums, stabilized against said gum formation by the presence of small amounts of a N,N'-di-cyclohexyl-p-phenylene diamine.

3. A motor fuel containing unsaturated hydrocarbons which normally tend to develop gums, stabilized against said gum formation by the presence of small amounts of a N,N'-di-methylcyclohexyl-p-phenylene diamine.

4. A motor fuel comprising gasoline containing gum-forming constituents and a small amount of a N,N'-di-cyclohexyl-p-phenylene diamine.

5. A method of stabilizing gasoline which normally tends to deteriorate and develop gums on storage which comprises adding thereto a small amount of a N,N'-di-cycloaliphatic-p-phenylene diamine.

6. A method of stabilizing gasoline which normally tends to deteriorate and develop gums on storage which comprises adding thereto a small amount of a N,N'-di-cyclohexyl-p-phenylene diamine.

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