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MOTOR FUEL

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This invention relates to the stabilization of motor fuels and particularly to the stabilization of cracked gasolines which tend to deteriorate and develop gums.

In particular, the present invention relates to the treatment of highly cracked gasolines or hydrocarbon motor fuel distillates of the type which are normally unstable, particularly with respect to gum formation on storage. It has been customary to treat motor fuels of this type with substances such as strong sulphuric acid, fuller's earth and the like to remove these gum-forming constituents. Such treatments remove a substantial amount of the unsaturated constituents in the gasoline and since these unsaturated constituents are partly responsible for the high antiknock properties of cracked gasoline, it is apparent that such treatment destroys some of the desirable qualities of cracked gasolines. In addition, these treatments result in a loss in volume of motor fuel. Although acid and/or clay treatment of motor fuels removes to some extent the gum forming constituents, often it is still necessary to further enhance the stability of such fuels by the addition of antioxidants. While most of the commercial antioxidants for this purpose are effective in inhibiting gum formation they possess the highly undesirable property of being color unstable, and discolor the fuel. Obviously this is highly detrimental to water white fuels as well as to many dyed fuels.

In the manufacture of cracked motor fuels it is commonly necessary to store the sour distillate prior to sweetening. Since the stored sour distillates tend to form gum it is often desirable to add an antioxidant to such stocks. However, most of the present commercial gum inhibitors are of the phenolic type and are therefore removed during the subsequent sweetening operations, necessitating the further addition of antioxidant to the sweetened distillate. It is highly desirable therefore to have a gum inhibitor which is not affected by the sweetening operation.

It is therefore an object of the present invention to provide a new class of color-stable organic materials that may be added to these gum-forming cracked gasolines, in small amounts, to inhibit or substantially retard the formation of gum and/or color therein.

Another object of the invention is to provide improved antioxidants for motor fuels which contain no acidic groups and are therefore not extracted by inorganic bases. Still another object of the invention is to provide antioxidants for motor fuels which are suitable for use in untreated, that is sour, fuels which are stored for appreciable time prior to doctor sweetening, and which will not be removed by subsequent sweetening treatment.

The amount of these inhibitors employed to stabilize a cracked gasoline will vary with the particular cracked gasoline to be treated but, in general, will vary from 0.05% to 0.001%. With some motor fuels, the amount used will be as low as 0.0005%. Even in these small concentrations, the class of inhibitors herein disclosed have proven to be very effective as gum inhibitors in cracked gasoline.

Our new antioxidants for cracked motor fuels are the condensation reaction product of an aldehyde or ketone with an organic diamino compound having two primary amino nitrogen atoms. These products are formed by reacting an organic primary diamine with a compound having the general formula



in which R may be an aliphatic, aryl, aralkyl, alkaryl, cycloaliphatic or a heterocyclic radical and R′ may be hydrogen or an aliphatic, aryl, aralkyl, alkaryl, cycloaliphatic or a heterocyclic radical. Examples of the aldehydes or ketones which may be employed in the condensation are crotonaldehyde, butyraldehyde, heptaldehyde, methyl hexylketone, furfural, acetaldehyde, isobutyraldehyde, acetone-phenone, benzaldehyde, acetone, vanillin, valeraldehyde, octylaldehyde, cinnamaldehyde, hexone, diisobutyl ketone and the like. Examples of organic diamino compounds which may be employed are phenylene diamine, ethylene diamine, amylene diamine, propylene diamine, 1,3 diamino butane, 1,4 diamino butane and others.

The above compounds may be prepared by slowly adding the diamino compound to a solution of the aldehyde or ketone and the compounds recovered by removing the solvent and water which is present by any suitable means. Suitable solvents are ether, benzene, alcohol and hexane, although other solvents may be used. The compounds may also be prepared by passing the vapors of the aldehyde or ketone and the polyamine compound into benzene and subsequently reducing the lower layer to remove water, benzol, etc. While it is preferable to add the finished compound to the fuel as such or in solution in some suitable solvent it is of course

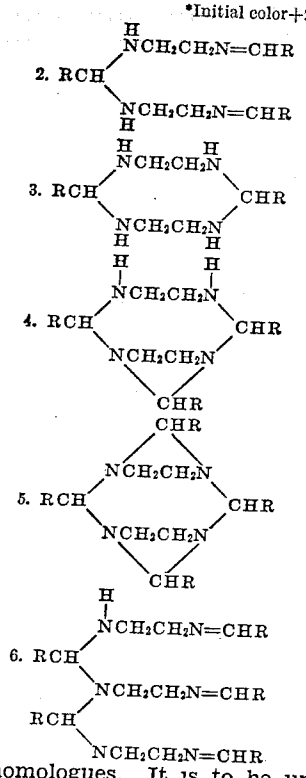
possible to form them in situ in the fuel by adding the reagents to the fuel, and subsequently removing any water resulting from the reaction.

We have not been able to determine the structure of the reaction products obtained, but believe them to be a mixture of condensation products since the determined molecular weights are greater than the calculated molecular weight, assuming the reaction product to be a single compound. Although we do not definitely know the exact structures of these compounds, we believe that the reaction product may be a mixture of compounds having the following structures, using the reaction product of ethylene diamine and an aldehyde,



as the example,

1. $RCH{=}NCH_2CH_2N{=}CHR$



2. $RCH(NCH_2CH_2N{=}CHR)_2$
3. $RCH(NCH_2CH_2N)_2CHR$
4. $RCH(NCH_2CH_2N)_2CHR$ with CHR bridge
5. $RCH(NCH_2CH_2N)_2CHR$ with CHR bridge
6. $RCH(NCH_2CH_2N{=}CHR)_2$ with $RCH(NCH_2CH_2N{=}CHR)$

and other homologues. It is to be understood that the foregoing formulae are given merely as examples of the possible structures of the constituents of the reaction products obtained when a diamine is chemically condensed with an aldehyde or ketone, and we do not intend to be held to any explanation or theory which we may expand with regard thereto.

The effectiveness of the inhibitors of the present invention in inhibiting gum formation and the inherent color stability of these inhibitors is demonstrated by the data in Table I. The data presented in this table were obtained in two storage tests at 90° F.; one to evaluate the gum inhibiting property of the class of compounds named herein, and the other to evaluate the color stability of the inhibitors. Test A made primarily for gum stability was made with an end-point cracked gasoline which had not been acid-treated, and Test B, made primarily for color stability, was carried out in a sulfuric acid-treated cracked gasoline.

Table I

Sample	Test A Storage period 26 weeks			Test B Saybolt color initial color+23	
	Percent inhibitor	Saybolt color*	Mgs. gum	19 wks.	28 wks.
Control	0.002	−2	10.0	+22	+20
Control+acetaldehyde-ethylene diamine condensation product	0.002	+2	1.5	+23	+23
Control+crotonaldehyde ethylene diamine condensation product	0.002	−2	3.8	+22	+21
Control+furfuraldehyde-ethylene diamine condensation product	0.002	−2	3.2	+22	+21
Control+heptaldehyde-ethylene diamine condensation product	0.002	−2	2.2	+21	+19
Control+butyraldehyde-ethylene diamine condensation product	0.002	−2	4.4	+21	+20
Control+butyraldehyde-o-phenylene diamine condensation product	0.002	−14	5.4	+15	+11
Control+methyl hexylketone-ethylene diamine condensation product	0.002	−2	1.5	+21	+19
Control+antioxidant I	0.002	1–1½ N. P. A.	2.8	Orange	Orange
Control+antioxidant II	0.002	1–1½ N. P. A.	3.7	Pink	Very pink

*Initial color+2 Saybolt.

Referring to the above table it will be noted that the condensation products of the present invention are effective not only in inhibiting gum formation, but are also effective in retaining the color of the gasoline. Antioxidants I and II are good commercial gum inhibitors but are themselves color unstable and cause a depreciation in the color of the fuel. Both samples of fuel containing antioxidants I and II went badly off color. In Tests A and B the fuel darkened too much to be measured by the A. S. T. M. method for determining the color of fuels by the Saybolt chromometer.

The gum formed was determined by the A. S. T. M. method D381–36 for determining the gum content of the gasoline. This test, which is described in detail in the September 1937 A. S. T. M. Standard on Petroleum Products and Lubricants (page 181), is a means of determining the amount of gum existent at the time of test in the fuel.

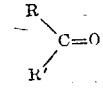
The development of color in fuels was determined by the A. S. T. M. method D156–35T which is described in detail on page 74 et seq. of the above publication. In this test the color of the fuel is measured by means of the Saybolt chromometer.

In addition to using the compounds indicated above as gum inhibitors in cracked gasoline, these agents may be used in blends of motor fuels containing substantial amounts of gum-forming cracked gasoline. In using the above mentioned

compounds to retard gum formation in cracked gasolines, we prefer to add the inhibitor to fresh gasoline or prior to the formation of gum.

We claim:

1. A motor fuel product comprising cracked hydrocarbon distillates of the character of gasoline which normally tend to deteriorate and develop gum, said product containing a small amount of the condensation product formed by reacting a compound selected from the class consisting of aldehydes and ketones free of hydroxy substituents and having the general formula



in which R is a radical selected from the group consisting of aliphatic, aryl, aralkyl, alkaryl, cyclo aliphatic and heterocyclic radicals, R′ is a substituent selected from the group consisting of hydrogen, an aliphatic radical, an aryl radical, an aralkyl radical, an alkaryl radical, a cyclo aliphatic radical and a heterocyclic radical with an organic primary diamine, said condensation product being added in quantities sufficient to retard the deterioriation of said cracked hydrocarbon distillates.

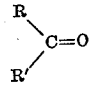
2. A motor fuel product comprising cracked hydrocarbon distillates of the character of gasoline which normally tend to deteriorate and develop gum, said product containing a small proportion of the product obtained by the condensation of an alkylene diamine and an aliphatic aldehyde.

3. A motor fuel product comprising cracked hydrocarbon distillates of the character of gasoline which normally tend to deteriorate and develop gum, said product containing a small proportion of the product obtained by the condensation of an alkylene diamine and an aromatic aldehyde.

4. A motor fuel product comprising cracked hydrocarbon distillates of the character of gasoline which normally tend to deteriorate and develop gum, said product containing a small proportion of the product obtained by the condensation of ethylene diamine and butyraldehyde.

5. A motor fuel product comprising cracked hydrocarbon distillates of the character of gasoline which normally tend to deteriorate and develop gum, said product containing a small proportion of the product obtained by the condensation of ethylene diamine and a methyl hexyl ketone.

6. The method of preserving cracked hydrocarbon distillates of the character of gasoline which normally tend to develop gum on storage which comprises incorporating therein a small proportion of the condensation product formed by reacting a compound selected from the class consisting of aldehydes and ketones free of hydroxy substituents and having the general formula



in which R is a radical selected from the group consisting of aliphatic, aryl, aralkyl, alkaryl, cyclo aliphatic and heterocyclic radicals, R′ is a substituent selected from the group consisting of hydrogen, an aliphatic radical, an aryl radical, an aralkyl radical, an alkaryl radical, a cyclo aliphatic radical and a heterocyclic radical with an organic primary diamine, said condensation product being added in quantities sufficient to retard the deterioriation of said cracked hydrocarbon distillates.

7. The method of preserving cracked hydrocarbon distillates of the character of gasoline which normally tend to develop gum on storage which comprises incorporating therein a small proportion of the product obtained by the condensation of an alkylene diamine and an aliphatic aldehyde.

8. The method of preserving cracked hydrocarbon distillates of the character of gasoline which normally tend to develop gum on storage which comprises incorporating therein a small proportion of the product obtained by the condensation of an alkylene diamine and an aromatic aldehyde.

9. The method of preserving cracked hydrocarbon distillates of the character of gasoline which normally tend to develop gum on storage which comprises incorporating therein a small proportion of the product obtained by the condensation of ethylene diamine and butyaldehyde.

10. The method of preserving cracked hydrocarbon distillates of the character of gasoline which normally tend to develop gum on storage which comprises incorporating therein a small proportion of the product obtained by the condensation of ethylene diamine and a methyl hexyl ketone.

11. A motor fuel product comprising cracked hydrocarbon distillates of the character of gasoline which normally tend to deteriorate and develop gum, said product containing a small proportion of the condensation product formed by reacting a diamino alkane with an aliphatic aldehyde.

12. A motor fuel product comprising cracked hydrocarbon distillates of the character of gasoline which normally tend to deteriorate and develop gum, said product containing a small proportion of the condensation product formed by reacting a diamino alkane with an aromatic aldehyde.

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