United States Patent [19]

Kerschner et al.

[11] **3,779,724**

[45] **Dec. 18, 1973**

[54] **NITROGEN-CONTAINING CARBOHYDRATE DERIVATIVES AND HYDROCARBON FUEL COMPOSITIONS CONTAINING SAME**

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[22] Filed: **Apr. 29, 1970**

[21] Appl. No.: **33,039**

[52] **U.S. Cl.** **44/63,** 44/71

[51] **Int. Cl.** **C10l 1/22**

[58] **Field of Search** 44/63, 71, 66

[56] **References Cited**

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[57] **ABSTRACT**

Compounds useful as additives in hydrocarbon fuels are prepared by reacting the lactone of a carbohydrate acid with a N-hydrocarbylhydrocarbylenediamine in which the amino groups are separated by two or three methylene groups. The reaction products are the isomeric amides of the carbohydrate acid and the hydrocarbylenediamine and also the heterocyclic compounds obtained when the foregoing amides cyclize with elimination of a mole of water. Hydrocarbon fuel compositions containing these additives exhibit enhanced carburetor detergency and rust inhibiting properties.

6 Claims, No Drawings

NITROGEN-CONTAINING CARBOHYDRATE DERIVATIVES AND HYDROCARBON FUEL COMPOSITIONS CONTAINING SAME

BACKGROUND OF THE INVENTION

Normally liquid hydrocarbon products such as fuels often require additives to improve their performance characteristics. Thus, in fuels such as gasoline, diesel fuel and jet fuel, various additives are employed to assist in maintaining cleanliness in the carburetor and fuel intake systems and to inhibit rust. The additives vary in effectiveness, and it is often necessary to use a number of additives in a single composition. Furthermore, many additives for hydrocarbon fuels are employed in concentrations that approach their limits of solubility. As a result, hydrocarbon fuel compositions containing such additives often exhibit poor stability and form gums on standing.

SUMMARY OF THE INVENTION

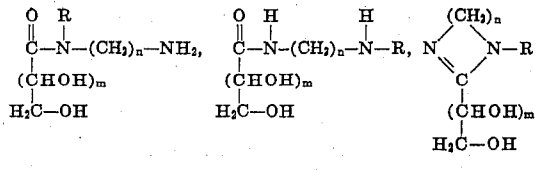
It is an object of this invention to provide additives which, when incorporated in normally liquid hydrocarbon fuels, impart desirable properties thereto.

It is another object of this invention to provide additives which, when incorporated in normally liquid hydrocarbon fuels, produce stable compositions.

It is yet another object of this invention to provide normally liquid hydrocarbon fuel compositions having enhanced carburetor and fuel intake system detergency properties as well as rust inhibiting characteristics.

Still other objects will appear hereinafter.

The foregoing objects are attained in accordance with our invention. In general, our invention consists of additives for normally liquid hydrocarbon fuels comprising nitrogen-containing carbohydrate derivatives selected from the group consisting of



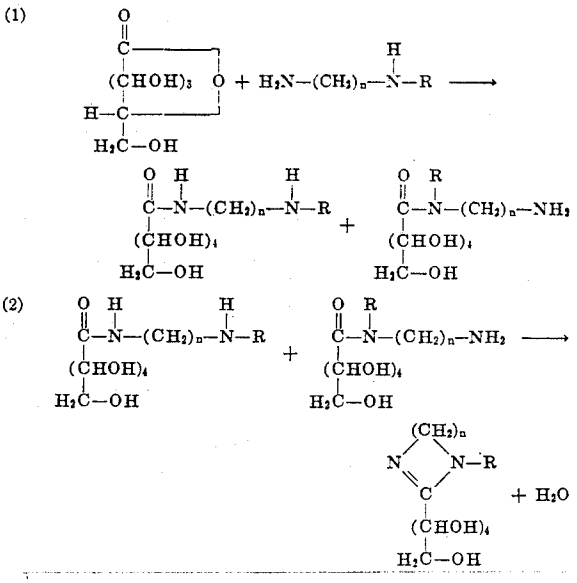
and mixtures thereof wherein n is an integer from 2 to 3, m is an integer from 2 to 4, and R is a hydrocarbyl group of about eight to about 40 carbons; and normally liquid hydrocarbon fuel compositions comprising a major proportion of a normally liquid hydrocarbon fuel and a minor proportion of the above additive.

Normally liquid hydrocarbon fuel compositions containing the additive compounds of this invention exhibit such desirable properties as enhanced carburetor and fuel intake system detergency and improved rust inhibition. In addition, liquid hydrocarbon fuel compositions containing the additive compounds of this invention are stable with little tendency toward gum formation. Other advantages of this invention will be apparent from the following description.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The normally liquid hydrocarbon fuel compositions of this invention are prepared by incorporating into a major proportion of a normally liquid hydrocarbon fuel a minor proportion of an additive which is a nitrogen-containing carbohydrate derivative. Examples of normally liquid hydrocarbon fuels that have desirable properties imparted thereto by the additives of this invention are gasoline, diesel fuel and jet fuel.

The novel nitrogen-containing carbohydrate derivatives of this invention are prepared by a procedure wherein the lactone of a carbohydrate acid is reacted with a diamine containing a hydrocarbyl group of one of the amino nitrogens and in which the amino groups are separated by either two, or three methylene groups. The reaction may be considered to proceed by a two step mechanism illustrated by the following:

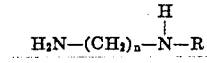


wherein n is an integer from 2 to 3 and R is a hydrocarbyl group of about eight to about 40 carbons.

Step (1) illustrates the formation of a mixture of isomeric amides by the opening of the lactone ring. Step (2) illustrates the intramolecular elimination of a mole of water by the mixture of isomeric amides to yield the compound having a heterocyclic ring. The isomeric amides from step (1) and the heterocyclic compound from step (2) as well as mixtures thereof, comprise the additive of this invention. However, the heterocyclic compounds are generally preferred.

The lactones of carbohydrate acids which are reacted with the diamines range in size from four to six carbons and may be gamma- or delta-lactones of acids of the isomeric tetroses, pentoses and hexoses. Examples of suitable lactones are the delta-lactone of gluconic acid, glucuronolactone, the gamma-lactone of mannonic acid, the gamma-lactone of gluconic acid, the gamma-lactone of arabonic acid, the delta-lactone of mannonic acid, the delta-lactone of arabonic acid, the gamma-lactone of threonic acid, the gamma-lactone of erythronic acid and the gamma-lactone of ribonic acid.

As disclosed above, the lactone of a carbohydrate acid is reacted with a diamine containing a hydrocarbyl group on one of the amino nitrogens and in which the amino groups are separated by either two or three methylene groups. The diamines have the general formula



wherein n is an integer from 2 to 3 and R is a hydrocarbyl group of about eight to 40 carbons and preferably about 12 to 30 carbons. R may be aliphatic, naphthenic or aromatic, or it may contain various mixtures of aliphatic, naphthenic and aromatic segments. The aliphatic and naphthenic segments may be either saturated or unsaturated. Examples of suitable diamines are N-(2-ethylhexyl)-1,3-propylenediamine; N-

dodecylethylenediamine; N-(2-nonenyl)-1,3-propylenediamine; N-(p-eicosylphenyl)-ethylenediamine; N-(4-heptylcyclohexyl)-ethylenediamine; N-(9-octadecenyl)-1,3-propylenediamine; N-(octaeicosylphenyl)-ethylenediamine; N-(4-butyl-2-cyclohexenyl)-ethylenediamine; N-(4-eicosykyclohexyl)-1,3-propylenediamine; N-(o-undecylphenyl)-ethylenediamine; N-(10-phenylstearyl)-1,3-propylenediamine and n-tallowylethylenediamine.

As stated above, the reaction of the lactone of a carbohydrate acid with the diamine may be stopped at step (1) where the product is the mixture of isomeric amides. Step (1) of the reaction may be carried out in an aprotic solvent such as toluene under sufficiently mild reaction conditions, e.g., below about 100°C, that elimination of water does not occur. Alternatively, the mixture of isomeric amides may be caused to undergo intramolecular elimination of a mole of water to cause formation of a heterocyclic ring as depicted in step (2) of the above series of equations. Step (2) may be carried out in an inert solvent such as toluene under conditions such as reflux, e.g., temperatures in excess of about 100°C, with simultaneous removal of the water formed as a by-product. When the amino groups of the diamine are separated by two methylene groups, the heterocyclic ring formed in step (2) is an imidazoline. When the amino groups of the diamine are separated by three methylene groups, the heterocyclic ring formed in step (2) is a tetrahydropyrimidine. The isomeric amides from step (1) and the heterocyclic compounds from step (2), as well as mixtures thereof, have been found to impart desirable properties such as enhanced carburetor and fuel intake system detergency and improved rust inhibition properties to hydrocarbon fuel compositions in which they have been incorporated. The heterocyclic compounds are generally preferred.

The normally liquid hydrocarbon fuel compositions containing the additives of this invention will vary in composition depending on the fuel and the properties it is desired to impart thereto. Generally, gasoline, diesel fuel and jet fuel compositions contain about 1 to about 15, and preferably about 3 to about 10, pounds per thousand barrels (PTB) of the additives of this invention. If necessary, the solubility of the additive in the hydrocarbon fuel may be increased by first dissolving the additive in a polar solvent which is miscible with the hydrocarbon fuel. An example of a suitable solvent for this purpose is a 50/50 mixture of toluene and 1-methoxy-2-propanol. If desired, the fuel compositions may also contain conventional additives such as antioxidants, octane improvers and metal scavengers. For example, it is contemplated that the additives of this invention may be employed in gasoline compositions which may or may not contain lead alkyls.

The efficacy of our additives in hydrocarbon fuel compositions is determined by subjecting the compositions to one or both of the following tests. The tests and their procedures are as follows.

Rust Test

Into a beaker are placed 30 ml. of distilled water and 300 ml. of the normally liquid hydrocarbon composition to be tested. The stirred mixture is heated to 100°F. A steel test specimen is inserted into the stirred, heated mixture and the mixture is stirred at 100°F for 24 hours. The steel specimen is then removed, allowed to drain and then washed with precipitation naphtha or isooctane. The percent of the surface of the steel test specimen that is covered by rust is determined.

Carburetor Detergency Test

Engine blow-by contaminants are generated in an engine and collected in a flask. At the end of the collection period the water phase is separated from the fuel phase, the latter being discarded. The water phase of the contaminants is used for the carburetor detergency evaluations.

The carburetor detergency test is run on a Cooperative Lubricants Research (CLR) engine, a single cylinder research engine manufactured by Laboratory Equipment Company. The contaminants are injected into the throttle body of a CLR engine running with a rich mixture and on which the throttle plate has been replaced by a 200 mesh stainless steel screen. The amount of deposits accumulated on the screen after 3 hours of engine operation indicates the detergency performance of the fuel. Experimental fuels, with reference and base fuel runs, are tested with the same batch of contaminants.

At the conclusion of the 3-hour run, the 200 mesh screen is removed and evaluated for contaminant accumulation. The reflectance of the screen, determined by means of a reflectance meter, is a measure of the amount of deposits accumulated on the screen. The higher the reflectance, the cleaner the screen, i.e., the lower the accumulation of deposits. The effectiveness of an additive is represented as the ratio, expressed as a percentage, of the average screen reflectance for the fuel containing the additive to the average screen reflectance for the base fuel containing no detergency additive. Thus an experimental additive that equals the performance of the base fuel will have an effectiveness of 100 percent, an experimental additive that performs at a lower level than the base fuel will have an effectiveness below 100 percent, and an experimental additive that performs at a higher level than the base fuel will have an effectiveness above 100 percent.

The following specific examples will serve to further illustrate our invention.

EXAMPLE I

In a round bottom flask fitted with a Dean-Stark trap and a reflux condenser are placed 45 g. (0.1 mole) of N-(10-phenylstearyl)-1,3-propylenediamine and 17.8 g. (0.1 mole) of the delta-lactone of gluconic acid in 40 ml. of toluene. The mixture is heated under reflux for 4.5 hours during which time 2.0 ml. of water are collected in the Dean-Stark trap. The theoretical amount of water for formation of the tetrahydropyrimidine ring is 1.8 ml. The solvent is removed by distillation under reduced pressure to yield 60.0 g. of dark brown, very viscous liquid. The product, 1-(10-phenylstearyl)-2-pentahydroxypentyltetrahydropyrimidine, is readily soluble in gasoline at room temperature to give stable solutions.

EXAMPLE II

In a round bottom flask fitted with a Dean-Stark trap and a reflux condenser are placed 45 g. (0.1 mole) of N-(10-phenylstearyl)-1,3-propylenediamine and 17.8 g. (0.1 mole) of the delta-lactone of gluconic acid in 40 ml. of toluene. The mixture is heated under reflux for 0.5 hour during which time no water is collected in the Dean-Stark trap. The solvent is removed by distillation

under reduced pressure to yield a tan, low-melting waxy solid. The product is the mixture of isomeric N-aminopropyl amides of gluconic acid.

EXAMPLE III

In a round bottom flask fitted with a Dean-Stark trap and a reflux condenser are placed 0.2 mole of N-(2-ethylhexl)-b 1,3-propylenediamine, 0.2 mole of the gamma-lactone of arabonic acid and 100 ml. of toluene. The reaction mixture is heated under reflux until the theoretical amount of water for formation of the tetrahydropyrimidine ring is collected in the Dean-Stark trap. The toluene is removed by distillation under reduced pressure to yield as product 1-(2-ethylhexyl)-2-tetrahydroxybutyltetrahydropyrimidine.

EXAMPLE IV

In a round bottom flask fitted with a Dean-Stark trap and a reflux condenser are placed 0.15 mole of N-(p-octaeicosylphenyl)-ethylenediamine, 0.15 mole of the gamma-lactone of mannonic acid and 150 ml. of toluene. The mixture is heated under reflux until the theoretical amount of water corresponding to cyclization to form the imidazoline ring is collected in the Dean-Stark trap. Toluene is removed by distillation under reduced pressure to yield the product 1-(p-octaeicosylphenyl)-2-pentahydroxypentylimidazoline.

EXAMPLE V

In a round bottom flask fitted with a Dean-Stark trap and a reflux condenser are placed 0.1 mole of the gamma-lactone of threonic acid, 0.1 mole of N-dodecylethylenediamine, and 60 ml. of benzene. The mixture is heated under reflux for 1 hour during which time no water is collected in the Dean-Stark trap. The benzene is removed by distillation under reduced pressure to yield as product the mixture of isomeric N-aminoethyl amides of threonic acid.

EXAMPLE VI

In a round bottom flask fitted with a Dean-Stark trap and a reflux condenser are placed 0.1 mole of the gamma-lactone of erythronic acid, 0.1 mole of N-(4-eicosylcyclohexyl)-1,3-propylenediamine and 50 ml. of toluene. The mixture is heated under reflux until the theoretical amount of water corresponding to cyclization to form the tetrahydropyrimidine ring is collected in the Dean-Stark trap. Toluene is removed by distillation under reduced pressure to yield a product of 1-(4-eicosylcyclohexyl)-2-trihydroxypropyltetrahydropyrimidine.

EXAMPLE VII

In a round bottom flask fitted with a Dean-Stark trap and a reflux condenser are placed 0.15 mole of the delta-lactone of mannonic acid, 0.15 mole of N-tallowylethylenediamine and 75 ml. of toluene. The mixture is heated under reflux until the theoretical amount of water corresponding to cyclization to form the imidazoline ring is collected in the Dean-Stark trap. Solvent is removed by distillation under reduced pressure to yield a product of 1-tallowyl-2-pentahydroxypentylimidazoline.

EXAMPLE VIII

In a round bottom flask fitted with a Dean-Stark trap and a reflux condenser are placed 0.2 mole of the gamma-lactone of gluconic acid, 0.2 mole of N-(4-butyl-2-cyclohexenyl)-ethylenediamine and 100 ml. of benzene. The mixture is heated under reflux for 1 hour during which time no water is collected in the Dean-Stark trap. Benzene is removed by distillation under reduced pressure to yield as the product a mixture of the isomeric N-aminoethyl amides of gluconic acid.

EXAMPLE IX

In a round bottom flask fitted with a Dean-Stark trap and a reflux condenser are placed 0.1 mole of the delta-lactone of arabonic acid, 0.1 mole of N-(o-undecylphenyl)-ethylenediamine and 65 ml. of toluene. The reaction mixture is heated under reflux until the theoretical amount of water for formation of the imidazoline ring is collected in the Dean-Stark trap. The toluene is removed by distillation under reduced pressure to yield as product 1-(o-undecylphenyl)-2-tetrahydroxybutylimidazoline.

EXAMPLE X

In a round bottom flask fitted with a Dean-Stark trap and a reflux condenser are placed 0.15 mole of the gamma-lactone of ribonic acid, 0.15 mole of N-(9-octadecenyl)-1,3-propylenediamine and 80 ml. of toluene. The mixture is heated under reflux for 0.5 hour driving time which no water is collected in the Dean-Stark trap. Toluene is then removed by distillation under reduced pressure to yield as a product a mixture of the isomeric N-aminopropyl amides of ribonic acid.

EXAMPLE XI

Two leaded gasoline (3 ml. TEL/gal.) compositions are prepared, one containing 6 PTB of the 1-(10-phenylstearyl)-2-pentahydroxypentyltetrahydropyrimidine of Example I and the other containing 6 PTB of the mixture of isomeric N-aminopropyl amides of gluconic acid obtained by reacting stoichiometric amounts of N-(10-phenylstearyl)-1,3-propylenediamine with the delta-lactone of gluconic acid without elimination of water as described in Example II. The gasoline compositions, which do not form on standing, are subjected to the carburetor detergency test. For comparison purposes, a base leaded gasoline (3ml. TEL/gal.) containing no additive other than lead alkyl is subjected to the carburetor detergency test.

In the carburetor detergency test to run on the base leaded gasoline, the reflectance of the 200 mesh screen is found to be 5.5 reflectance units. Thus a reflectance of 5.5 units is assigned an effectiveness of 100 percent. The 200 mesh screen from a carburetor detergency test on the gasoline composition containing 6 PTB of 1-(10-phenylstearyl)-2-pentahydroxypentyltetrahydropyrimidine has a reflectance of 9.8 units and the composition accordingly has a 178 percent effectiveness. The 200 mesh screen from a carburetor detergency test run on the gasoline composition containing 6 PTB of the mixture of isomeric N-aminopropyl amides of gluconic acid has a reflectance of 7.0 and the composition thus has a 127 percent effectiveness.

When the gasoline composition containing 6 PTB of 1-(10-phenylstearyl)-2-pentahydroxypentyltetrahydropyrimidine is subjected to the rust test, the steel test specimen is found to have 25 percent of its surface covered by rust. In comparison, when the rust test is carried out on the base leaded gasoline, the steel test specimen has 70 percent of its surface covered by rust.

EXAMPLE XII

Several leaded gasoline (3 ml. TEL/gal.) compositions containing the additives of this invention are prepared and subjected to the carburetor detergency test and the rust test. The concentrations of the additives in the leaded gasoline are as follows: 15 PTB of the 1-(p-octaeicosylphenyl)-2-pentahydroxypentylimidazoline of Example IV; PTB of the mixure of isomeric N-aminoethyl amides of threonic acid of Example V; 4 PTB of the mixture of isomeric N-aminoethyl amides of gluconic acid of Example VIII; and 9 PTB of the 1-(2-ethylhexyl)-2-tetrahydroxybutyltetrahydropyrimide of Example III. In every case, the gasoline compositions containing the additives of this invention are stable and have better carburetor detergency and rust inhibiting properties than does a base leaded gasoline (3ml. TEL/gal.) containing no additive other than the lead alkyl.

EXAMPLE XIII

Several unleaded gasoline compositions containing the additives of this invention are prepared and subjected to the carburetor detergency test and the run test. The concentrations of the additives in the unleaded gasoline are as follows: 14 PTB of the 1-(4-eicosylcyclohexyl)-2-trihydroxypropyltetrahydropyrimidine of Example VI; 10 PTB of the 1-tallowyl-2-pentahydroxypentylimidazoline of Example VII; 2 PTB of the mixture of isomeric N-aminopropyl amides of ribonic acid of Example X; and 3 PTB of the 1-(o-undecylphenyl)-2-tetrahydroxybutylimidazoline of Example IX. For purposes of comparison, a base unleaded gasoline containing no additive is subjected to the carburetor detergency test and the rust test. The unleaded gasoline compositions containing the additives of this invention, in each case, do not tend to form gum on standing and have superior carburetor detergency and improved rust inhibiting properties relative to the base unleaded gasoline.

EXAMPLE XIV

A number of diesel fuel compositions are prepared containing the additives of this invention. These compositions, and a base diesel feul containing no additives, are subjected to the rust test. The concentrations of the additives in the diesel fuel are as follows: 1 PTB of the mixture of isomeric N-aminopropyl amides of gluconic acid of Example II; 8 PTB of the 1-(10-phenylstearyl)-2-pentahydroxypentyltetrahydropyrimidine of Example I; 15 PTB of the 1-(p-octaeicosylphenyl)-2-pentahydroxypentylimidazoline of Example IV; 6 pTB of the mixture of isomeric N-aminoethyl amides of threonic acid of Example V; 4 PTB of the 1-(o-undecylphenyl)-2-tetrahydroxybutylimidazoline of Example IX; and 10 of the 1-(4-eicosylcyclohexyl)-2-trihydroxypropyltetrahydropyrimidine of Example VI. The steel test specimens from rust tests on diesel fuel compositions containing the foregoing additives have less surface rust than does the steel test specimen from a rust test run on the base diesel fuel containing no additive. Furthermore, the diesel fuel compositions containing the additives are stable and do not tend to form gum on standing.

EXAMPLE XV

A number of jet fuel compositions containing additives of this invention are prepared. These jet fuel compositions, as well as a base jet fuel containing no additive, are subjected to the rust test. The concentrations of the additives in the jet fuel are as follows: 7 PTB of the 1-(10-phenylstearyl)-2-pentahydroxypentyltetrahydropyrimidine of Example I; 2 PTB of the 1-(2-ethylhexyl)-2-tetrahydroxybutyltetrahydropyrimidine of Example III; 13 PTB of the 1-tallowyl-2-pentahydroxypentylimidazoline of Example VII; 3 PTB of the mixture of isomeric N-aminoethyl amides of gluconic acid of Example VIII; 9 PTB of the 1-(o-undecylphenyl)-2-tetrahydroxybutylimidazoline of Example IX; and 5 PTB of the mixture of isomeric N-aminopropyl amides of ribonic acid of Example X. These jet fuel compositions are stable on standing. The steel test specimens from rust tests on the jet fuel compositions containing the above additives have less surface rust than does the steel test specimen from a rust test run on the base jet fuel containing no additive.

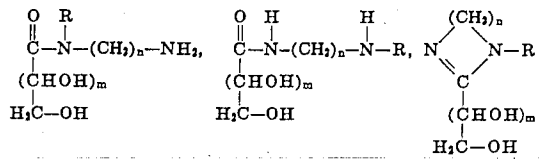
EXAMPLE XVI

A leaded gasoline (3 ml. TEL/gal.) composition containing 8 PTB of a 50/50 mixture of the 1-(10-phenylstearyl)-2-pentahydroxypentyltetrahydropyrimidine of Example I and the mixture of isomeric N-aminopropyl amides of gluconic acid of Example II is prepared. The gasoline composition does not form gum on standing and has better carburetor detergency and rust inhibiting properties than does a base leaded gasoline containing no additive other than the lead alkyl.

While this invention has been described above with respect to certain preferred embodiments thereof, it will be understood by those skilled in the art that various changes and modifications may be made without departing from the spriit and scope of the invention.

We claim:

1. A normally liquid hydrocarbon fuel composition comprising a major proportion of a normally liquid hydrocarbon fuel and about 1 to about 15 pounds per thousand barrels of said composition of an additive selected from the group consisting of



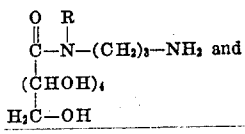
and mixtures thereof wherein *n* is an integer from 2 to 3, *m* is an integer from 2 to 4, and R is a hydrocarbyl group of about eight to about 40 carbons.

2. The composition of claim **1** wherein the normally liquid hydrocarbon fuel is selected from the group consisting of gasoline, diesel fuel and jet fuel.

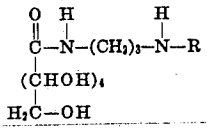
3. The composition of claim **2** wherein R is a hydrocarbyl group of about 12 to about 30 carbons.

4. The composition of claim **3** wherein the concentration of the additive is about 3 to about 10 pounds per thousand barrels of said composition.

5. The composition of claim **4** wherein the additive is a mixture of

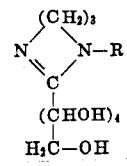


and



wherein R is a 10-phenylstearyl group.

6. The composition of claim 4 wherein the additive is a compound having the formula



wherein R is a 10-phenylstearyl group.

* * * * *

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,779,724 Dated December 18, 1973

Inventor(s) Paul M. Kerschner, et al.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, line 4, "of" should read - - on - - ; column 2, line 6, the comma should be deleted; column 2, line 39, after "(2)" there should be a comma. Column 3, line 7, the portion of the word reading "eicosykyclohexy should read - - eicosylcyclohexyl - - ; column 3, line 10, the prefix "n" should read - - N - - . Column 5, line 8, "ethylhexl)-b" should read - - ethylhexyl)- - - ; column 6, line 42, after "form" the word - - gum - - should be inserted; column 6, line 47, after "test" the word "to" should be deleted. Column 7, line 9, the portion reading "PTB of the mixure should read - - 1 PTB of the mixture - - ; column 7, line 24, the word "run" should read - - rust - - ; column 7, line 53, "pTB" should read - - PTB - - ; column 7, line 56, after "10" - - PTB - - should be inserted.

Signed and sealed this 9th day of April 1974.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents

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