United States Patent Office

3,347,645

Patented Oct. 17, 1967



3,347,645

# MULTIPURPOSE GASOLINE ADDITIVE

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No Drawing. Filed Dec. 20, 1963, Ser. No. 332,233

10 Claims. (Cl. 44—63)

This invention concerns a multipurpose gasoline additive package, and more particularly, a multipurpose additive package that does not significantly promote dispersions of water in gasoline.

Various nitrogen-containing derivatives of high molecular weight alkenylsuccinic anhydride have become known as sludge dispersants for lubricating oils and are described in U.S. Patents 3,018,247, 3,018,250 and 3,018-291. A particularly effective derivative of this general type is prepared by reacting an alkenylsuccinic anhydride with a polyamine, e.g., tetraethylene pentamine, as described in Australian patent application No. 63,803, filed Aug. 22, 1960. Recently, it was found that additives of the last-named type can be further improved in their sludge dispersing effectiveness in lubricating oil by converting the polyamine into a 2-imidazoline which is condensed with the alkenylsuccinic anhydride. These additives are also useful in gasoline. They reduce crankcase slude and piston varnish. They are good corrosion inhibitors and improve the stability of gasoline in storage.

Although these additives are effective in gasoline, there is a serious problem that is occasioned in their use. During transport and storage, gasoline commonly contacts water bottoms. Ordinarily, in storage two distinct phases separate: a clear gasoline phase and a water layer.

The additives described above promote a dispersion of water in the gasoline. This is undesirable for many reasons, for example, the entrained water commonly causes carburetor icing that results in engine power losses and engine stalling.

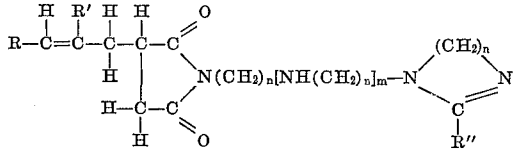
In addition, these dispersant additives promote a gasoline-in-water emulsion; the resulting creamy additive gasoline-in-water emulsion is undesirable in that it results in a waste of gasoline and additive and presents problems in disposing of the water bottoms containing high concentrations of gasoline.

It is therefore an object of this invention to provide a multipurpose addditive package (containing the above-described imidazoline-alkenylsuccinic anhydride condensation products) that effects an essentially complete separation of gasoline and water.

The object of this invention is attained by using the imidazoline-alkenylsuccinic anhydride in combination with a benzene sulfonic acid and an ethoxylated dimeric acid.

The additive package comprises a multipurpose additive prepared by condensing an imidazoline with an alkenylsuccinic anhydride in combination with a benzene sulfonic acid and an ethoxylated dimeric acid. In a preferred embodiment of this invention, a solvent oil is included in the package.

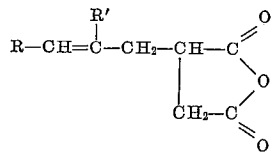
The additive that is active in reducing crankcase sludge and in inhibiting corrosion is a derivative of an alkenylsuccinic anhydride and has the following formula:



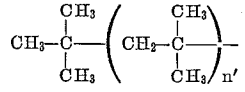


wherein R and R′ are selected from the group consisting of hydrogen and hydrocarbon radicals provided that at least one of said R and R′ is a hydrocarbon radical and the total number of carbon atoms in R and R′ combined is about 40 to 250; R″ is an aliphatic hydrocarbon radical of 1 to 30 carbon atoms; $n$ is 2 to 3 and $m$ is 0 to 10.

The alkenylsuccinic anhydrides can be readily prepared by reacting maleic anhydride with an organic compound having a double bond at an end to thereby give compounds of the general formula:

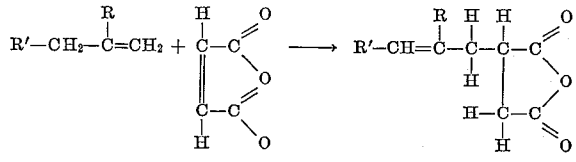


wherein R and R′ can be hydrogen, or hydrocarbon radicals which can be either substituted (e.g., chlorinated or sulfurized) or unsubstituted, including aliphatic, acyclic, aromatic radicals, etc., although at least one of said R and R′ must be a hydrocarbon group. The total of R and R′ will generally contain 40 to 250, preferably 70 to 120, carbon atoms. Primarily because of its ready availability and low cost, the alkenyl portion of the molecule is preferably obtained by reacting with the maleic anhydride a polymer of a $C_2$ to $C_5$ monoolefin, said polymer generally having a molecular weight of about 700 to 3,000 e.g., about 800 to 1,300. A particularly preferred example of such an olefin polymer is polyisobutylene. In this case, R′ will be hydrogen, while R will be the radical:



where $n'$ is determined by the molecular weight of the polyisobutylene being used.

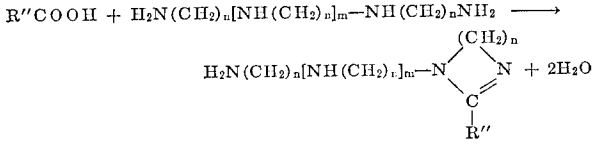
The preparation of alkenylsuccinic anhydride is known in the art, for example, see U.S. 3,018,250, column 3, lines 57 to 71, Example 1. Generally, about equal molar proportions of maleic anhydride and the olefinic material are simply heated together. Inert solvents, such as toluene, xylene, etc., can be used as diluents to lower the viscosity of the reaction product in the case of a very viscous alkenyl material to permit easier subsequent filtration of the reaction product. The solvent can then be later removed by evaporation. Or, in some cases where the diluent is high-boiling and not objectionable in the final end use, the diluent can be simply left in the reaction product. This preparation of the alkenylsuccinic anhydride is illustrated by the following equation:



wherein R and R′ have the meanings previously given.

The imidazoline that is reacted with the alkenyl-

succinic anhydride can be prepared by a condensation reaction of a carboxylic acid and an aliphatic polyamine as illustrated by the following equation using a monocarboxylic acid:



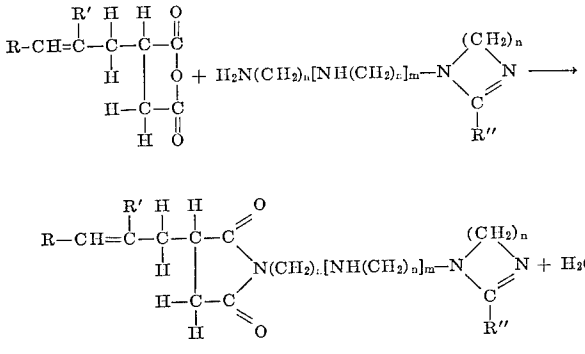
wherein R'' is a $C_1$ to $C_{30}$, preferably a $C_1$ to $C_{18}$ aliphatic hydrocarbon radical, either saturated or unsaturated, of a fatty acid; *n* is 2 or 3; and *m* is 0 to 10, preferably 0 to 3. In place of the monocarboxylic acid illustrated by the above equation, dicarboxylic acids can also be used, in which case both carboxylic acid groups can react with a terminal amine groups of two separate polyamine molecules.

Examples of operable acids include acetic acid, fumaric acid, capric acid, adipic acid, lauric acid, oleic acid, linoleic acid, stearic acid, etc. Acetic acid is particularly preferred since it forms an imidazoline with a minimum of carbon atoms. Thus, since the acid does not appear to contribute very much to the final product, aside from permitting the imidazoline formation, the lower the molecular weight of the acid the more effective the final product appears to be in sludge dispersing ability per weight of final product. In other words, the higher acids appear to contribute bulk without substantial improvement, so as to lessen the effectiveness of the final product on a weight basis, although such higher acids are operable.

Examples of the polyamines operable in the above reaction include diethylene triamine, tetraethylene pentamine, octaethylene nonamine, tetrapropylene pentamine, etc.

The imidazoline-forming reaction between the acid and the polyamine can be carried out by simple mixing of substantially stoichiometric proportions of said acid and polyamine, followed by heating to reflux and the removal of the water of condensation. An invert solvent, such as heptane or toluene, can be used, if desired, as a water-entraining agent in order to aid in the removal of the water of reaction. The solvent can then be removed later by evaporation.

The third step in forming the product of the present invention involves the reaction of the imidazoline with the alkenylsuccinic anhydride. This reaction is represented by the following equation:



wherein R, R', R'', *m* and *n* have the meanings previously mentioned. This third and last step of the reaction represented above is preferably carried out using an equi-molar proportion of the two reactants by heating to refluxing and removing the water of condensation. An inert solvent can again be used, as in the first two stages, in preparing the final product.



As mentioned before, the above-described additives promote a water haze in gasoline and an additive-gasoline emulsion in water.

Many known dehazing additives proved to be unsuccessful in dissipating the water haze in gasoline. Although some tended to clear the gasoline, the results were not satisfactory. Likewise, many known demulsifiers were unsuccessful in breaking the additive and gasoline in water emulsion. In short, many combinations of dehazers and demulsifiers proved to be unsatisfactory.

It has now been discovered that a particular combination of additives causes a complete separation of gasoline and water. Neither additive used alone satisfactorily clears either the gasoline or the water phase. However, when used in combination, the additives effect an essentially complete separation of water and gasoline.

The combination of additives employed to cause complete separation of gasoline and water comprises a benzene sulfonic acid and an ethoxylated dimeric acid.

Suitable benzene sulfonic acids include alkyl benzene sulfonic acids wherein the alkyl group contains from 1 to 30 carbon atoms, and preferably from 8 to 16 carbon atoms. It is preferred that the alkyl group be branch-chained and unsubstituted, however, straight-chained alkyl groups containing substituent groups are believed to be satisfactory. The most preferred alkyl benzene sulfonic acids are those wherein the alkyl group is unsaturated, e.g., dodecyl benzene sulfonic acid. These additives can be prepared by methods well known to the art.

The ethoxylated polymeric acid is prepared by reacting a polyalkylene glycol with a polymeric carboxylic acid. Suitable carboxylic acids include those having from 14 to 60 carbon atoms per carboxyl group; preferred acids include dilinoleic and trilinoleic acids. A very satisfactory acid for use in preparing the ethoxylated polymeric acid is a mixture of polymerized fatty acids predominanting in trilinoleic acid. Such acids may be produced as by-products still-residues in the manufacture of sebacic acid by the distillation of castor oil. The residue is an amber-colored viscous residue containing long chain polycarboxylic acids, having an acid number between 140 and 165, an iodine number of between 30 and 60, and is the nonvolatile material remaining from vacuum distilling at 270° C. under 4 mm. Hg pressure the by-product acids obtained in the preparation of sebacic acids from castor oil in the presence of an alkali. These materials are fully described in U.S. Patents 2,471,230, 2,267,269, and 2,470,849.

The residue comprises monomers, dimers, trimers, and higher polymers in the ratio of from about 45 to 55 wt. percent of a monomers and dimers fraction having a molecular weight in the range of from about 300 to 600, and from about 55% to 45 wt. percent of a higher polymer fraction having a molecular weight above 600.

This residue is reacted with a polyalkylene glycol to obtain the additive employed in this invention. Polyethylene glycol is preferred but polyglycols made from alkylene compounds having from 2 to 7 carbon atoms are suitable. The polyalkylene glycol should have a molecular weight of from 200 to 800, preferably 300 to 500.

The polymeric carboxylic acid is reacted with the polyalkylene glycol (stoichiometric amounts) in the presence of from about 0.2 to 0.4 wt. percent of an alkaline catalyst, e.g. soda ash, sodium hydroxide, or the like. The catalyst should be added after the temperature of the reactants has been rapidly raised to about 300° F. After the catalyst addition, the temperature should then be raised to about 500° F. and kept there for from 2 to 4 hours.

In a preferred embodiment of this invention, the additive package contains a solvent oil to reduce the amount of deposits in the intake manifold.

The oil should boil in the range of from 350° to 800° F. at 10 mm. of Hg and preferably from 400° F. to 700° F. The oil should have a viscosity within the range of from 45 SSU/210° F. to 150 SSU/210° F. Typical inspection for an oil of this type is as follows:

TABLE I

| | |
|---|---|
| Gravity, ° API | 28.8 |
| Sulfur, wt. percent | 0.40 |
| Neutralization No. D974 | 0.02 |
| Aniline point, ° F. | 273.5 |
| ASTM distillation, 10 mm. Hg vacuum: | |
| IBP, ° F. | 353 |
| 10% Point, ° F. | 464 |
| 50% Point, ° F. | 534 |
| 90% Point, ° F. | 626 |
| FBP, ° F. | 694 |
| Conradson Carbon Residue | 0.1 |
| Vis/210° F., SSU | 60.7 |

The imidazoline alkenylsuccinic anhydride condensation product is employed in gasoline in a small amount sufficient to reduce engine deposits. The amount needed varies, depending upon the gasoline, the presence of other additives etc., but generally in the range of from 1 to 500 pounds per 1,000 barrels of gasoline, and preferably, in the range of from 15 to 100.

The combination of benzene sulfonic acid and the ethoxylated dimeric acid is employed in a minor amount sufficient to effect an essentially complete separation of water and gasoline. This amount varies, depending upon the particular water bottoms contacted. The combination should be employed in gasoline in a concentration of from 10 to 120 p.p.m. A larger amount can be employed, but is usually not necessary. A preferred range and a range that is suitable for most purposes is from 25 to 40 p.p.m.

The combination of benzene sulfonic acid and the ethoxylated dimeric acid is operable over a wide range of relative proportions. The benzene sulfonic acid should constitute from 30 to 90 wt. percent of the combination, preferably 45 to 75%.

The imidazoline alkenylsuccinic anydride condensation product, the benzene sulfonic acid and the ethoxylated dimeric acid are viscous materials and can be blended prior to being added to gasoline by blending at a temperature of about 130 to 150° F. to form an essentially homogenous blend. This blend should comprise from 91 to 93 wt. percent of the condensation product and from 9 to 7 wt. percent of the combination of benzene sulfonic acid and the ethoxylated dimeric acid wherein the sulfonic acid constitutes from 30 to 90 wt. percent, preferably 45 to 75 wt. percent of the combination.

If intake valve deposits are encountered, one may dissolve the above-described blend in a solvent oil such as that oil described in Table I. The resulting gasoline composition should contain from 0.1 to 1 vol. percent, preferably 0.5 vol. percent, of the oil to reduce intake valve deposits.

It is sometimes desirable to employ a solvent containing at least 50% aromatics, e.g. toluene or the like, rather than the aliphatic solvent described in Table 1. The aromatic solvents are not as effective in reducing deposit formation, but the additive blend of this invention is more stable in the aromatic solvents. Since the additive blend can be more easily dissolved in gasoline if it is in a solvent solution, one finds an advantage in using the aromatic solvent where the solvent-additive solution must be stored prior to admixture with gasoline; no precipitation occurs from the aromatic solvent solution whereas some is observed with the use of an aliphatic solvent.



The gasolines to which the additive blend of the invention is added may also contain other additives such as lead alkyl antiknock additives, anti-icing additives, e.g. hexylene glycol and the like, and other additives commonly employed in fuels.

The following specific additives were tested to illustrate the efficacy of the instant invention:

*Additive A*

*Part 1.*—Alkenylsuccinic anhydride was prepared as follows:

2700 grams of polyisobutylene of 1,1000 molecular weight (Staudinger) was added to a flask containing 270 grams of maleic anhydride. These reactants were then heated at a temperature of about 485° F. for about 19 hours, cooled to about 60° C., diluted with about 50 wt. percent toluene, based on the total weight of reactants, filtered through Hyflo and then the toluene was evaporated overnight on a steam bath. The toluene was used simply to reduce the viscosity of the reaction product to permit easier filtering. The recovered reaction product was a tacky material of amber color, and had a saponification number of 67.2 mg. KOH/gm. of reaction product.

*Part 2.*—An imidazoline was prepared as follows:

300 grams (5 moles) of glacial acetic acid was added to a flask containing 945 grams (5 moles) of tetraethylene pentamine and 125 gm. xylene. The contents of the flask were heated to reflux at atmospheric pressure and the water of reaction was collected in a Dean-Stark trap unil 152 gm. of water had been so collected. The refluxing took about 16 hours. The product was then cooled. The water-entraining agent, i.e. xylene, was stripped from said product with $N_2$ blowing while heating on a steam bath. The resulting imidazoline was a dark, amber-colored oil.

*Part 3.*—The alkenylsuccinic anhydride and imidazoline were reacted as follows:

50.2 grams of the imidazoline product of Part 2 above was reacted with 300 grams of the alkenylsuccinic anhydride product of Part 1, in the presence of 70 grams of toluene, by heating together at a temperature of about 123° C. for about 8 hours until about 5 ml. of $H_2O$ had collected in a Dean-Stark trap. The product was then stripped of toluene (the water entraining agent) by blowing with nitrogen while heating on a steam bath. The final product was a dark-colored, viscous material having a reddish cast.

*Additive B*

A commercial grade of dodecylbenzene sulfonic acid was employed in the tests described hereinafter.

*Additive C*

The preferred ethoxylated dimeric acid of this invention is made by reacting polyethylene glycol having a molecular weight of 400 with a residue prepared as described in U.S. Patent 2,471,230, special attention being directed to Col. 1, line 46 through column 2 line 10. See also U.S. 2,723,233, where the use of the material is described.

66.93 grams of the residue (molecular weight about 1200) and 33.07 grams of polyethylene glycol having a molecular weight of 400 were charged into a flask and air-blown. The temperature was rapidly raised to 300° F. and 0.025 weight percent soda ash was added. The temperature of the reactants was then raised to 500° F. and maintained at this temperature for approximately 2½ hours.

The above-described additives were tested in a gasoline of the following specification.

TABLE II

*Base gasoline inspections*

| | |
|---|---|
| ASTM Distillation, Method D–86: | |
| 20% Boiling point, ° F. | 131 |
| 55% Boiling point, ° F. | 212 |
| 96% Boiling point, ° F. | 356 |
| Final boiling point, ° F. | 395 |
| ASTM Gum, mg./100 ml. | 2 |
| ASTM Breakdown time, min. | 300 |
| FIA Analysis: | |
| Vol. percent saturates | 50 |
| Vol. percent olefins | 28.8 |
| Vol. percent aromatics | 21.2 |
| Tetraethyl Lead, cc./gal. | 1.22 |
| Research octane No. (RON) | 94.3 |
| Motor octane No. (MON) | 84.8 |

*Example 1.*—4.5 ml. of alkaline water bottoms were added to a 450 ml. sample of the gasoline described in Table II. The blend was then agitated in a Waring Blendor for one minute at 3600 r.p.m. A water haze formed in the gasoline, but the water separated from the gasoline soon after the agitation was stopped.

*Example 2.*—A solution was prepared consisting of one gram of Additive A in 100 ml. of toluene. To several 450 ml. samples of the gasoline described in Table II, 4.5 ml. of alkaline water bottoms and various amounts of the Additive A toluene solution were added. Each sample was agitated in a Waring Blendor as described in Example 1. A stable water haze was formed in the gasoline. Most of the samples cleared within six hours, However, the water that separated out contained gasoline and various amounts of Additive A. Moreover, slight agitation (that which can be expected in the normal storage and transportation of gasoline) caused the formation of a stable water haze in the gasoline again.

It is thus seen that Additive A (an effective multipurpose additive) promotes the formation of a stable water haze in gasoline and thus a portion of the additive is lost from the gasoline by promoting an emulsion of Additive A and gasoline in water.

*Example 3.*—Samples were prepared comprising 450 ml. gasoline (Table II), 4.5 ml. alkaline water bottoms, Additive A (1.02 g./gal.), and Additive B (dodecylbenzene sulfonic acid-various concentrations in toluene solution). Each sample was agitated as in the tests described in the preceding examples. Most of the samples cleared within six hours, however, an emulsion of gasoline and Additive A in water remained at the interface of the gasoline and water phases. Moreover, as in Example 2, mild agitation formed another stable water haze in gasoline that was slow in disappearing. In short, Additive B used alone had little effect in promoting a complete separation of the gasoline and water.

*Example 4.*—Samples were prepared comprising 450 ml. of gasoline containing 4.5 ml. of alkaline water bottoms, Additive A toluene solution (about 90 lbs./1000 barrels), and various amounts of Additive C. Each sample was agitated as described in the preceding examples.

Most of the samples cleared after six hours, but an emulsion formed at the interface. Moreover, mild agitation cause a haze to again form in the gasoline.

The above examples show that Additive A (an effective multipurpose additive) causes the formation of a haze in the gasoline and promotes a gasoline and additive emulsion in water. The examples also show that neither Additive B nor Additive C, used alone, obviates these problems. The following example illustartes the efficacy of the additive combination of this invention.

*Example 5.*—Several gasoline samples (similar to gasoline described in Table II) were prepared containing the following ingredients. The oil was employed to dissolve the ingredients prior to blending with the gasoline.



| | Parts by weight |
|---|---|
| Additive A | 23.03 |
| Additive B | 1.59 |
| Additive C | 0.64 |
| Solvent oil (Table I) | 74.74 |

This additive blend was added to 450 ml. samples of gasoline containing 4.5 ml. alkaline water bottoms; the blend was added in various amounts, e.g. 0.875 to 0.2 g. per sample.

The samples were agitated in a Waring Blendor for one minute at 3600 r.p.m.

The sample cleared within six hours (some within one hour). In contrast with the results observed from the tests described in Examples 2 to 4:

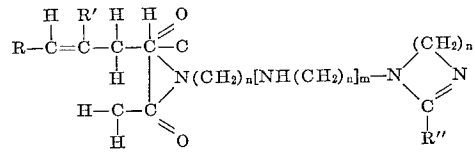
(1) There was no emulsion at the interface or in the water phase.

(2) Mild agitation or the sample did not result in the formation of a stable haze. The water was dispersed in the gasoline, but an immediate separation was observed.

What is claimed is:

**1.** A multipurpose gasoline additive blend that does not significantly promote a dispersion of water in gasoline; said blend consisting essentially of:

from 90 to 95 parts by weight of a multipurpose derivative of an alkenylsuccinic anhydride having the following formula:



wherein R and R′ are selected from the group consisting of hydrogen and hydrocarbon radicals provided that at least one of said R and R′ is a hydrocarbon radical and the total number of carbon atoms in R and R′ combined is in the range of about 40 to 250; R″ is an aliphatic hydrocarbon radical having in the range of 1 to 30 carbon atoms; *n* is 2 to 3 and *m* is 0 to 10; and

from 10 to 5 parts by weight of the following combination:

an alkyl benzene sulfonic acid wherein the alkyl group contains in the range of from 1 to 30 carbon atoms; and

the reaction product of a polyalkylene glycol of a molecular weight in the range of about 200 to 800 with an amber-colored viscous residue containing long chain polycarboxylic acids, having an acid number between 140 and 165, an iodine number of between 30 and 60, said residue being the nonvolatile material remaining from vacuum distilling at 270° C. under 4 mm. Hg pressure, the by-product acids obtained in the preparation of sebacic acid from castor oil by treatment with an alkali;

said alkyl benzene sulfonic acid constituting from 30 to 90 weight percent of said combination of alkyl benzene sulfonic acid and reaction product.

**2.** An additive blend according to claim **1** wherein said alkyl group in said alkyl benzene sulfonic acid contains from 8 to 16 carbon atoms.

**3.** An additive blend according to claim **1** wherein said alkyl benzene sulfonic acid is dodecylbenzene sulfonic acid.

**4.** An additive blend according to claim **1** wherein said polyalkylene glycol is polyethylene glycol.

**5.** An additive blend according to claim **1** wherein said blend is dissolved in a solvent selected from the class

consisting of aliphatic solvent oils and aromatic solvent oils.

6. An additive blend according to claim 1 wherein said benzene sulfonic acid constitutes from 45 to 75 weight percent of the combination.

7. An additive blend according to claim 1 wherein the alkylene group in said polyalkylene glycol has from 2 to 7 carbon atoms.

8. An improved gasoline to which has been added a minor amount of the additive blend defined by claim 1 sufficient to inhibit the formation of engine deposits.

9. An improved gasoline to which has been added sufficient of the additive blend defined by claim 1 to impart to said gasoline from 1 to 500 pounds of said alkenyl succinic anhydride derivative per 1,000 barrels of gasoline.

10. An improved gasoline as defined by claim 9 wherein the alkyl benzene sulfonic acid in said additive blend is dodecyl benzene sulfonic acid.



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UNITED STATES PATENT OFFICE

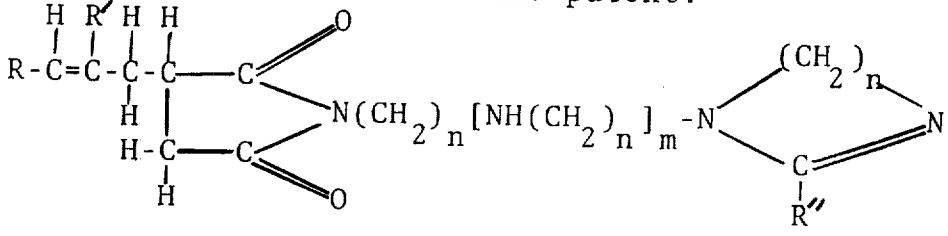
# CERTIFICATE OF CORRECTION

Patent No. 3,347,645 October 17, 1967

Gerhard J. Pietsch et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 8, lines 30 to 40, the formula should appear as shown below instead of as in the patent:



Signed and sealed this 26th day of November 1968.

(SEAL)

Attest:

Edward M. Fletcher, Jr.
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents