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3,485,601 FLUOBORATE SALTS OF HYDROCARBYL ALKYLENE POLYAMINES

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No Drawing. Filed June 24, 1966, Ser. No. 560,080
Int. Cl. C101 1/30, 1/22; C07f 5/02

U.S. Cl. 44—58

5 Claims

ABSTRACT OF THE DISCLOSURE

A hydrocarbon fuel containing novel polyamine fluoborates which find use as detergents and deicers in said fuels.

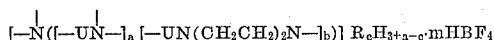
This invention concerns relatively high molecular weight novel polyamine fluoborates which find use as detergents and deicers in fuels.

Fuels used today include a wide variety of additives to improve the properties of the fuel during storage, handling and use, so as to increase the efficiency of operation of the internal combustion engine. The limitations on the additives are manifold. Not only must the additive provide the necessary improvement(s), but it also must be compatible with the other additives which are present in the fuel. Furthermore, since the fuel is ultimately consumed in the engine, it is essential that the additive in no wise reduce the fuel's efficiency as a source of energy or contribute to deposits which would reduce the efficiency of the engine.

Recently, new detergents were found which were particularly effective in fuels. These detergents are described in copending application Ser. No. 488,775, filed Sept. 20, 1965. The detergents are N-aliphatic hydrocarbon substituted alkylene polyamines, wherein the aliphatic hydrocarbon substituent is usually a long branched chain primarily saturated hydrocarbon free of aromatic unsaturation.

Pursuant to this invention, the fluoborate salts of high molecular weight branched chain hydrocarbon N-substituted alkylene polyamines are provided which are superior detergents and dispersants as well as antiicing agents in hydrocarbonaceous fuels for internal combustion engines. The compositions of this invention also provide other advantages in the fuel. The detergents used in the fuel compositions of this invention have molecular weights in the range of about 450 to 10,000, more usually in the range of 450 to 5,000 and preferably in the range of 450 to 3,500. Particularly preferred are polyisobutylene alkylene polyamines having from 2 to 5 nitrogen atoms and being in the range of about 450 to 1,500 molecular weight.

For the most part, the detergent antiicing compositions are described by the following formula:



The above symbols are defined as follows:

U—alkylene of from 2 to 6 carbon atoms

a—an integer of from 0 to 10

b—an integer of from 0 to 1

a+2b—an integer of from 1 to 10

c—an integer or fractional number of from 1 to 5, but per molecule less than the number of nitrogen atoms in the molecule

m—an integer of from 1 to 2, usually 1

R—hydrocarbon radical relatively free of aromatic unsaturation of from about 400 to 5,000 molecular weight

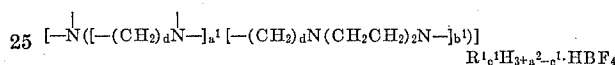
The alkylene radical, indicated as U, will have from 2 to 6 carbon atoms, the nitrogen atoms connected by U being separated by at least 2 carbon atoms. (By alkylene

is intended the normal meaning that the valences be on different carbon atoms.) The alkylene group may be straight chain or branched. Various alkylene groups include ethylene, 1,2-propylene, trimethylene, pentamethylene, hexamethylene, 2-methyl 1,3-propylene, etc.

The hydrocarbon radical indicated by R may have a variety of structures and may be aliphatic or alicyclic, and is generally free of aromatic unsaturation. Conveniently, the hydrocarbon radical may be a polymer of olefins of from 2 to 6 carbon atoms (if ethylene is used, the ethylene will be copolymerized with an olefin of at least 3 carbon atoms) or may be derived from naturally occurring products of relatively high molecular weight, e.g., naphthenic bright stock.

The alkylene polyamines may be derived from various amino compounds such as ethylene diamine, diethylene triamine, tetraethylene pentamine, octaethylene nonamine, nonaethylene decamine, 2-aminoethyl piperazine, 1,3-propylene diamine, 1,2-propylene diamine, tetraethylene diamine, etc.

The detergent-antiicing compositions having branched chain aliphatic hydrocarbon substituents will generally be of the following formula:



The above symbols are defined as follows:

a¹—an integer of from 0 to 5

b¹—an integer of from 0 to 1

a¹+2b¹—an integer in the range of from 1 to 5

c¹—an integer or fractional number in the range of 1 to 3, generally per molecule there being fewer R¹ groups than nitrogen atoms

d—an integer in the range of 2 to 3

R¹—a branched chain aliphatic radical of from about 400 to 3,000 molecular weight

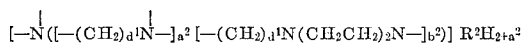
As indicated, R¹ is an aliphatic branched chain hydrocarbon radical. R¹ may be aliphatically saturated or have aliphatic unsaturation, e.g., olefinic. Generally, R¹ will have from 0 to 1 sites of aliphatic unsaturation. By branched it is intended that on the average there be at least 1 branch per 6 carbon atoms along the chain, preferably at least 1 branch per 4 atoms along the chain and particularly preferred that there be from 0.5 to 1 branch per carbon atom along the chain (at least one branch per two carbon atoms along the chain). Preferably, the branches will be of from 1 to 2 carbon atoms, i.e., methyl or ethyl.

The branched chain aliphatic hydrocarbon radical is readily prepared by polymerizing olefins of from 2 to 6 carbon atoms (copolymerizing an olefin of from 3 to 6 carbon atoms with ethylene) and preferably polymerizing olefins of from 3 to 6 carbon atoms, particularly isobutylene.

In most instances a single compound will not be used as a reactant in the preparation of the detergent-antiicing composition. That is, mixtures will be used in which one or two compounds will predominate and the average composition or molecular weight is indicated. For example, tetraethylene pentamine prepared by the polymerization of aziridine or reaction of dichloroethylene and ammonia will have both lower and higher members, e.g., triethylene tetramine and pentaethylene hexamine, but the composition will be mainly tetraethylene pentamine and the empirical formula of the total composition will closely approximate that of tetraethylene pentamine. Similarly, the molecular weight reported for the branched chain aliphatic hydrocarbon group is an average for a mixture which is sharply peaked when graphing the number average molecular weight distribution. Also, when the nitrogen atoms of the alkylene polyamines are not equiv-

alent, substitution on different nitrogen atoms will afford different compounds.

As is evident from the above formulae, the alkylene polyamines used in the preparation of the fluoborate salts may have only one hydrocarbon substituent or may be polysubstituted with hydrocarbon radicals. The mono-substituted alkylene polyamine compositions will have the following formula:



The above symbols are defined as follows:

a^2 —an integer of from 0 to 5, preferably of from 0 to 4
 b^2 —an integer of from 0 to 1, preferably 0 when a^2 is greater than 0

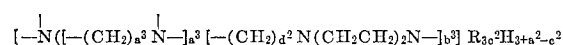
$a^2 + 2b^2$ —an integer of from 1 to 5

d^1 —an integer of from 2 to 3

R^2 —a branched chain aliphatic hydrocarbon radical derived from polymerizing olefins of from 3 to 6 carbon atoms, preferably of from 3 to 4 carbon atoms, and particularly preferred of propylene and isobutylene and having a molecular weight in the range of 400 to 3,000, preferably 400 to 2,500

Illustrative compounds within the above formula are as follows: N-polyisobutenyl ethylene diamine, N-polypropenyl ethylene diamine, N-poly(1-butenyl) ethylene diamine, N-(alternating copolymer of ethylene and isobutylene) ethylene diamine (alternating copolymers of ethylene and isobutylene may be achieved by the cationic polymerization of 4-methylpentene-1), N-polypropenyl 2-aminoethylpiperazine, N-polyisobutenyl 2-aminoethylpiperazine, N-polypropenyl diethylene triamine, N-polyisobutenyl diethylene triamine, N-poly(1-pentenyl) diethylene triamine, N-polypropenyl trimethylene diamine, N-polyisobutenyl trimethylene diamine, N-polypropenyl di(trimethylene) triamine, N-polyisobutenyl di(trimethylene) triamine, N-polyisobutenyl 1,2-propylene diamine, N-polyisobutenyl di(1,2-propylene) triamine, N-polypropenyl triethylene tetramine, N-(alternating copolymer of ethylene and isobutylene) triethylene tetramine, N-polypropenyl tetraethylene pentamine, N-polyisobutenyl tetraethylene pentamine, N-polyisobutenyl pentaethylene hexamine, etc.

The polyhydrocarbon radical substituted alkylene polyamine compositions used in the formation of the fluoborate salts have the following formula:



The above symbols are defined as follows:

a^3 —an integer of from 0 to 5, preferably an integer of from 1 to 4

b^3 —an integer of from 0 to 1, preferably 0 when a^3 is greater than 0

$a^3 + 2b^3$ —an integer of from 1 to 5

c^2 —a fractional or whole number in the range of 1 to 3, generally per molecule there are fewer R^3 groups than nitrogen atoms

d^2 —an integer of from 2 to 3

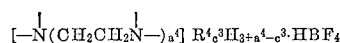
R^3 —a branched chain aliphatic hydrocarbon radical either free of or having aliphatic unsaturation, e.g., olefinic and of from 400 to 3,000 molecular weight, preferably of from 400 to about 2,500 molecular weight

(As indicated by the above formula, the number of hydrocarbon substituents need not be a whole number when averaged over the total composition; generally, a mixture will be obtained containing mono-, di- and tri- or higher substituted molecules averaging out to a fractional or whole number.)

Illustrative compounds coming within the above formula are as follows: N,N'-di(polypropenyl) diethylene triamine, N,N'-di(polyisobutenyl) diethylene triamine, N,N'-di(polyisobutenyl) triethylene tetramine, N,N'-di(polypropenyl) tetraethylene pentamine, N,N'-di(polyisobutenyl) tetraethylene pentamine, N,N',N''-tri(polyiso-

butenyl) tetraethylene pentamine, N,N'-di(polyisobutenyl) 2-aminoethylpiperazine, N,N'-di(poly-1-butenyl) triethylene tetramine, N,N'-di-polyisobutenyl di-(trimethylene) triamine, etc.

The preferred detergent-antiicing compositions are those having the straight chain alkylene polyamines, particularly ethylene diamine and polyethylene polyamines. These compositions have the following formula:



The above symbols are defined as follows:

a^4 —an integer of from 1 to 5, preferably of from 1 to 4

c^3 —an integer or fractional number of from 1 to 3, preferably of from 1 to 2, generally per molecule there being fewer R^4 groups than nitrogen atoms

R^4 —a branched chain aliphatic hydrocarbon radical of from 400 to 3,000 molecular weight, preferably of from 400 to 2,500 molecular weight, and, particularly preferred, either polypropenyl or polyisobutenyl

The detergent-antiicing compositions are readily prepared by combining an aliphatic or alicyclic halide with the desired amine in the proper mole proportions. The halide is prepared from the hydrocarbon by halogenation: ionically or free radically. The amine thus obtained is then combined with aqueous fluoboric acid in the stoichiometric amount for the desired product in the presence of an aromatic hydrocarbon. The water and hydrocarbon are azeotroped off, leaving the desired fluoborate salt.

As already indicated, the hydrocarbon groups may be prepared by ionic or free radical polymerization of olefins of from 2 to 6 carbon atoms (ethylene must be copolymerized with another olefin) to an olefin of the desired molecular weight. The olefins which find use are ethylene, propylene, isobutylene, 1-butene, 1-pentene, 3-methyl-1-pentene, 4-methyl-1-pentene, etc., preferably propylene and isobutylene.

As previously indicated, there should be at least one branch per 6 carbon atoms along the chain and preferably at least one branch per 4 carbon atoms along the chain. The preferred olefins, propylene and isobutylene, have from 0.5 to 1 branch per atom along the hydrocarbon chain.

Alternatively, various naturally occurring materials may be used which have the desired molecular weight and aliphatic or alicyclic character.

The halogen may be introduced into the hydrocarbon molecule by various means known in the art. Most readily, either chlorine or bromine (halogen of atomic number 17-35) may be introduced by the free radical catalyzed halogenation of the hydrocarbon, or ionic addition to olefinic unsaturation. Various free radical catalysts may be used, such as peroxides, azo compounds, bromine, iodine, as well as light. Ionic catalysts are exemplified by ferric chloride. Methods of halogenation are well known in the art and do not require extensive exemplification or illustration here.

The amount of halogen introduced will depend on the particular hydrocarbon used, the desired amount of amine to be introduced into the molecule, the particular alkylene amine used, and the halogen used. The amount of halogen introduced will generally be in the range from about 1 to 5 halogen atoms per molecule, depending on the reactivity of the resulting halide. On a weight percent basis, the amount of halide will generally range from about 1 to 25, more usually from about 1 to 10.

The haloalkylhydrocarbon and alkylene polyamine or polyalkylene polyamine may be brought together neat or in the presence of an inert solvent, particularly a hydrocarbon solvent. The inert hydrocarbon solvent may be aliphatic or aromatic. Also, aliphatic alcohols may be used by themselves or in combination with another solvent, when capable of dissolving the reactants.

The reaction may be carried out at room temperature (20° C.), but elevated temperatures are preferred. Usually, the temperature will be in the range of from about

100° to 225° C. Depending on the temperature of the reaction, the particular halogen used, the mole ratios and the particular amine, as well as the reactant concentrations, the time may vary from 1 to 24 hours, more usually from about 3 to 20 hours. Times greatly in excess of 24 hours do not particularly enhance the yield and may lead to undesirable degradation. It is therefore preferred to limit the reaction time to fewer than 24 hours.

The mole ratio of halohydrocarbon to alkylene amine will generally be in the range from about 0.2 to 10 moles of alkylene amine per mole of halohydrocarbon, more usually 0.5 to 5 moles of alkylene amine per mole of halohydrocarbon. The mole ratio will depend upon the amount of halogen present in the halohydrocarbon, the particular halogen and the desired ratio of hydrocarbon to amine. If complete suppression of polysubstitution of the alkylene polyamines is desired, then large mole excesses of the amine will be used.

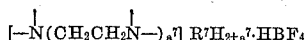
Small amounts of residual halogen in the final composition are not deleterious. Generally, the residual halogen as bound halogen will be in the range of 0 to 10 weight percent of the composition. Small amounts of halogen may be present as the hydrohalide salt of the hydrocarbon substituted alkylene polyamines.

Generally, the hydrocarbons used will have aliphatic unsaturation. In particular instances, the amines may react in a way resulting in the elimination of hydrogen halide, introducing further aliphatic unsaturation into the hydrocarbon radical. Therefore, the hydrocarbon radicals usually will be olefinically unsaturated. However, the olefinic unsaturation does not significantly affect the utility of the product, and when available, saturated aliphatic halide may be used.

After the reaction has been carried out for a sufficient length of time, the reaction mixture may be extracted with a hydrocarbon medium to free the product from any low molecular weight amine salt which has formed. The product may then be isolated by evaporation of the solvent. Further separation from unreacted hydrocarbon or purification may be carried out as desired, e.g., chromatography.

The fluoborates are prepared by reaction of the N-aliphatic hydrocarbyl alkylene diamine with fluoboric acid which may be formed by reacting boron trifluoride with hydrogen fluoride or hydrofluoric acid with boric oxide. The fluoboric acid is commercially available as an aqueous solution of approximately 48 percent concentration and will generally be used as such. Upon addition of the diamine to the aqueous solution of the fluoboric acid, the fluoborate salt is formed in a moderately exothermic reaction. Benzene may then be added or be included initially and the water removed by azeotropic distillation.

The particularly preferred detergent-antiicing compositions which find use in fuels have the following formula:



The above symbols are defined as follows:

a^7 —an integer of from 1 to 4

R^7 —a branched chain aliphatic hydrocarbon radical of from about 450 to 1,500 molecular weight, preferably polypropylene or polyisobutylene

Sufficient illustrations of the compounds within the above formula have already been indicated.

The detergent-antiicing agent will generally be employed in a hydrocarbon base fuel. The additive may be formulated as a concentrate, using a suitable hydrocarbon alcohol solvent boiling in the range of about 150° to 400° F. Preferably, an aromatic hydrocarbon solvent is used, such as benzene, toluene, xylene, or higher boiling aromatics or aromatic thinners. Aliphatic alcohols of about 3 to 8 carbon atoms, such as isopropanol, isobutylcarbinol, n-butanol and the like, in combination with hydrocarbon solvents are also suitable for use with the additive. In the concentrate, the amount of the additive will

be ordinarily at least 10 percent by weight and generally not exceed 70 percent by weight.

As already indicated, the additives of this invention provide deicing or antistalling properties as well as detergent. Also, some rust inhibition or corrosion inhibition is also obtained.

Generally, the additives will be present in at least 15 parts per million, usually at least 50 parts per million and generally not greater than about 0.1 weight percent. Most frequently, excellent results will be obtained with concentrations of from about 100 to 5,000 p.p.m.

The additives of this invention are particularly useful with volatile fuels having Reid vapor pressures above about 9. These are generally winter gasolines employed in northern areas where the Reid vapor pressure of the fuel is generally between about 9 and 13.5.

In gasoline fuels, other fuel additives may also be included such as antiknock agents, e.g., tetramethyl lead or tetraethyl lead. Also included may be lead scavengers such as aryl halides, e.g., dichlorobenzene or alkyl halides, e.g., ethylene dibromide.

A nonvolatile light mineral lubricating oil, such as petroleum spray oil is also a suitable additive for the gasoline compositions used with the additives of this invention and its use is preferred. These oils are believed to act as a carrier for the detergent-deicer and assist in removing and preventing deposits. They are employed in amounts from about 0.05 to 0.5 percent by volume, based on the final gasoline composition.

The following examples are offered by way of illustration and not by way of limitation.

EXAMPLE I

Into a reaction vessel was introduced 21 kg. of chloropolyisobutylene (approximately 950 molecular weight, 3.9% chlorine) in benzene as a 60 weight percent solution, heated to 120° F. and 8 kg. of a mixture having an average composition of tetraethylene pentamine added. After adding 8.1 kg. of n-butanol, the mixture was heated to 212° F. and held at that temperature for 1 hour while benzene was taken overhead. The temperature was slowly raised to 325° F. until a total of 13.4 kg. of volatiles was taken overhead. The temperature was allowed to drop to 250° F. and 50 lbs. of toluene added. When the temperature reached 170° F., 1.5 gals. of absolute ethanol and 3 gals. of hot water were added. The mixture was stirred and allowed to settle. The organic phase was separated and the above procedure repeated two more times. During the fourth washing, an emulsion formed and 1 gal. of ethanol and 1 gal. of n-butanol were added and the phases allowed to separate. The aqueous phase was discarded and the organic phase distilled. An aliquot of the residue was analyzed. Mol. wt. (ThermoNAM—A Differential Vapor Pressure Technique), 1,384; percent N, 3.95, 3.82.

In a second reaction vessel was introduced 17.6 g. of a 50 weight percent aqueous solution of fluoboric acid and 125 g. of benzene. To this mixture was slowly added 246 g. of a toluene solution containing 47.1 weight percent of the polyisobutylene tetraethylene pentamine prepared above. The water was removed by azeotropic distillation, the residue weighing 285 g.

EXAMPLE II

Into a reaction vessel was introduced 44 lbs. of chlorinated polyisobutylene (approximately 600 molecular weight, percent Cl, 4.9) in 23 lbs. of benzene, and the mixture heated to 120° F. To this mixture was added 17.6 lbs. of ethylene diamine and 17.8 lbs. of n-butanol, and the temperature raised to 212° F. and held for 1 hr. while taking benzene overhead. The temperature was then slowly raised to 322° F. while taking further volatile materials overhead. After allowing the mixture to cool to 200° F., 54 lbs. of toluene was added and when the temperature dropped to 160° F., 9.5 lbs. of n-butanol

and 3 gals. of hot water were added. After stirring and allowing the mixture to settle, the aqueous solution was withdrawn and the washing was repeated by adding 3 gals. of hot water and 2 lbs. of n-butanol. The washing with warm water was repeated 3 times and the volatile materials were then distilled off. Analysis of the product showed mol. wt. (ThermoNAM), 678; percent N, 2.89, 2.90.

Into a second reaction vessel was introduced 17.6 g. of a 50 weight percent aqueous fluoboric acid solution, 29.5 g. of benzene and then slowly 135.2 g. of the above product containing 47.5 weight percent active material. The water was removed by the further addition of 200 ml. of benzene, then distilling benzene-water, leaving the desired fluoborate salt.

In order to demonstrate the effectiveness of the compositions of this invention as antistalling/antiicing additives, the following test was carried out. In this test, a pump is used to pull an air-fuel mixture (95-100 percent relative humidity, 40° F.) through a simulated carburetor. The apparatus is sized and operated to simulate the operation of a carburetor on a 1965 slant-six 225-cubic inch Plymouth engine operating at 1500 r.p.m. with an air-fuel mixture of 14:1 and a manifold vacuum of 10-12" Hg. Evaporation of the gasoline in the glass tube cools the moist air with resulting ice formation on the perforated "throttle plate." The ice on the plate restricts the flow of the air-fuel mixture, causing the pressure to change. The time that additives in the fuel delay formation of ice on the plate as measured by a pressure increase of 4" Hg is called the induction period and is a measure of the effectiveness of the additive.

TABLE I

Additive Ex.	Conc., p.p.m.	Induction period, seconds	No. of determinations
II-----	100	42	16
Base fuel-----		21	40

In order to demonstrate the excellent detergency of the compositions of this invention, the following test was carried out. Using a Plymouth L-head engine, a clean glass throttlebody is run on base fuel for 1 hour with all blowby gases ducted to the carburetor inlet and with a rich air-fuel ratio the conditions are as follows: jacket temperature -160° F.; oil temperature—approximately 130° F.; engine speed—500 r.p.m. and accelerates to 2,000 r.p.m. five successive times every 7½ mins.; load—none. This is followed by running the engine on the additive containing fuel for 4 hours with no blowby gases ducted to the carburetor and with the normal air-fuel ratio. A comparison of the throttlebody at the end of the first 1 hour period and at the end of the run with the additive containing fuel is determined as the percent of deposits removed by the additive fuel.

Usually, the run is carried out at least 4 times and the results reported as an average of all the runs.

The following table compares the base fuel with the fluoborate salts as well as the parent amine.

TABLE II

Additive Ex.	Conc., p.p.m.	Percent cleanup	No. of determinations
5 I-----	30	79	6
II-----	30	83	6
Amine of Ex. II-----	30	62	7
Base fuel-----		35	4

The above tests demonstrate that the detergent deicers of this invention provide excellent protection to the engine in significantly reducing stalling and maintaining engine parts free of deposits. Quite surprisingly, not only do the fluoborate salts provide deicing, but they are equivalent to or superior to the parent amines as detergents.

As will be evident to those skilled in the art, various modifications on this invention can be made or followed, in the light of the foregoing disclosure and discussion, without departing from the spirit or scope of the disclosure or from the scope of the following claims.

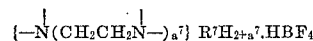
I claim:

1. A fuel composition comprising a liquid hydrocarbon distillate fuel for use in an internal combustion engine and in an amount sufficient to provide antiicing properties and detergency, a composition of the formula:



wherein U is alkylene of from 2 to 6 carbon atoms, *a* is an integer of from 0 to 10, *b* is an integer of from 0 to 1, *a*+2*b* is an integer of from 1 to 10, *c* is an integer or fractional number of from 1 to 5, but per molecule less than the number of nitrogen atoms in the molecule, *m* is an integer of from 1 to 2 and R is a hydrocarbon radical relatively free of aromatic unsaturation of from about 400 to 5,000 molecular weight.

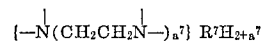
2. A fuel composition comprising a liquid hydrocarbon distillate fuel for use in an internal combustion engine and in an amount sufficient to provide antiicing properties and detergency, a composition of the formula:



wherein *a*⁷ is an integer of from 1 to 4 and R⁷ is a branched chain aliphatic hydrocarbon radical of from about 450 to 1,500 molecular weight.

3. A fuel composition according to claim 1, wherein from 0.05 to 0.5% by volume of a nonvolatile light mineral lubricating oil is present.

4. A fuel composition according to claim 2 containing a detergent of the formula:



wherein the symbols are as defined as in claim 2.

5. A fuel composition according to claim 4, wherein R⁷ is polyisobutylene.

References Cited

UNITED STATES PATENTS

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DANIEL E. WYMAN, Primary Examiner

Y. H. SMITH, Assistant Examiner

U.S. Cl. X.R.

44-72

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,485,601 Dated December 23, 1969

Inventor(s) ENVER MEHMEDBASICH

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

Col. 1, line 5, after "94530" insert --assignor to Chevron Research Company, San Francisco, Calif., a corporation of Delaware.--

The assignment was recorded in the Patent Office on October 3, 1969, on Reel 2537, Frame 346.

SIGNED AND
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JUL 14 1970

(SEAL)

Attest:

Edward M. Fletcher, Jr.
Attesting Officer

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Commissioner of Patents