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(54) Deposit-resistant motor fuel composition containing an additive which lowers the use of octane boosters.

(57) Motor fuel compositions, which are haze free and which show improved deposit resistance, Ori control and valve deposit control in comparison with typical commercial fuel compositions, include the reaction product obtained by reacting at a temperature of 30 ° C-200 ° C

(a) about 1 mole of a dibasic acid anhydride of the formula

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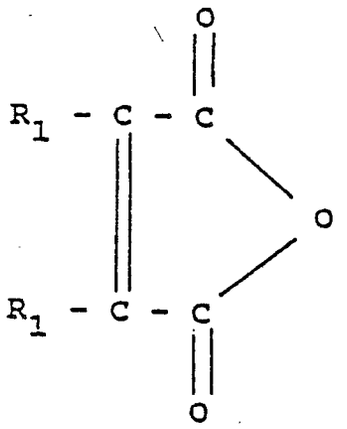
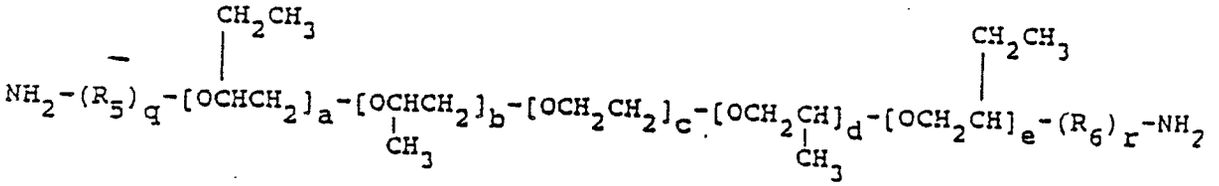


where R_1 is either H or a C_1-C_5 alkyl radical;

(b) 1-2 moles of a polyoxyalkylene diamine of the formula



where R_5 and R_6 are C_1-C_{12} alkylene groups, q and r are integers having a value of 0 or 1, c has a value from about 5-150, b + d has a value from about 5-150, and a + e has a value from about 2-12; and

(c) 1-2 moles of a hydrocarbyl polyamine which may be either

(i) a hydrocarbyl polyamine of the formula

$R_2(NH\text{-}R_3)_x\text{ - }NH_2$

where R_2 is n alkyl radical having from about 1-24 carbon atoms, R_3 is an alkylene radical having from about 1-6 carbon atoms, and x has a value from about 1-10, or

(ii) a n-alkyl-alkylene diamine of the formula

$R_4\text{-}NH\text{-}(CH_2)_n\text{-}NH_2$

where R_4 is an aliphatic hydrocarbon radical having from about 1-24 carbon atoms and n has a value from about 1-6;

REACTION PRODUCT ADDITIVE ORI-INHIBITED AND DEPOSIT RESISTANT MOTOR FUEL COMPOSITION

This invention relates to a gasoline-soluble reaction product, to a concentrate comprising the reaction product dissolved in a hydrocarbon solvent, and to a haze-free, deposit resistant and ORI-inhibited motor fuel composition comprising the reaction product.

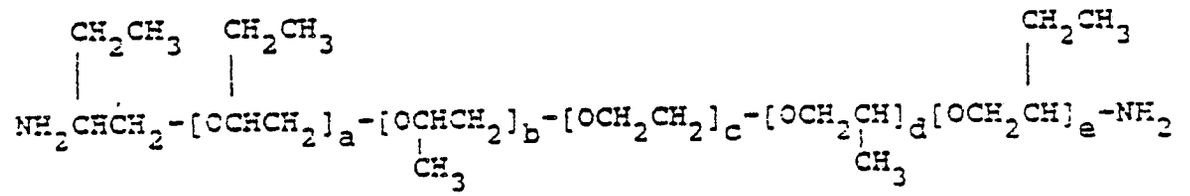
Combustion of a hydrocarbon and hydrocarbonaceous motor fuel in an internal combustion engine generally results in the formation and accumulation of deposits on various parts of the combustion chamber as well as on the fuel intake and exhaust systems of the engine. The presence of deposits in the combustion chamber seriously reduces the operating efficiency of the engine. First, deposit accumulation within the combustion chamber inhibits heat transfer between the chamber and the engine cooling system. This leads to higher temperatures within the combustion chamber, resulting in increases in the end gas temperature of the incoming charge. Consequently, end gas auto-ignition occurs, which causes engine knock. In addition, the accumulation of deposits within the combustion chamber reduces the volume of the combustion zone, causing a higher than design compression ratio in the engine. This, in turn also results in serious engine knocking. A knocking engine does not effectively utilize the energy of combustion. Moreover, a prolonged period of engine knocking will cause stress fatigue and wear in vital parts of the engine. The above-described phenomenon is characteristic of gasoline powered internal combustion engines. It is usually overcome by employing a higher octane gasoline for powering the engine, and hence has become known as the engine octane requirement increase (ORI) phenomenon. It would therefore is highly advantageous if engine ORI could be substantially reduced or eliminated by preventing or modifying deposit formation in the combustion chambers of the engine.

Another problem common to internal combustion engines relates to the accumulation of deposits in the carburetor which tend to restrict the flow of air through the carburetor at idle and at low speed, resulting in an overrich fuel mixture. This condition also promotes incomplete fuel combustion and leads to rough engine idling and engine stalling. Excessive hydrocarbon and carbon monoxide exhaust emissions are also produced under these conditions. It would therefore be desirable from the standpoint of engine operability and overall air quality to provide a motor fuel composition which minimizes or overcomes the above-described problems.

A third problem common to internal combustion engines is the formation of intake valve deposits. Intake valve deposits interfere with valve closing and eventually result in valve burning. Such deposits interfere with valve motion and valve sealing, and in addition reduce volumetric efficiency of the engine and limit maximum power. Valve deposits are usually a result of thermal and oxidative unstable fuel or lubricating oil oxidation products. Hard carbonaceous deposits collect in the tubes and runners that conduct the exhaust gas recirculation (EGR) gases. These deposits are believed to be formed from exhaust particles which are subjected to rapid cooling while mixing with the air-fuel mixture. Reduced EGR flow can result in engine knock and NO_x emission increases. It would therefore be desirable to provide a motor fuel composition which minimizes or overcomes the formation of intake valve deposits.

Deposit-inhibiting additives for use in motor fuel compositions are well known in the art. For example:

Co-assigned U. S. Pat. Appl. Serial No. 000,253, filed January 2, 1987, (D#78,650) (Sung et al.) discloses a novel polyoxyalkylene diamine compound of the formula:



where c has a value from about 5-150, b + d has a value from about 5-150, and a + e has a value from about 2-12. Motor fuel compositions comprising the novel polyoxyalkylene diamine, alone or in combination with a polymer/copolymer additive are also disclosed.

Co-assigned U. S. 4,689,031 (Sung) discloses an additive composition useful in improving the storage stability of middle distillate fuel oils, the additive prepared by reacting (i) a hydrocarbon-substituted mono primary amine or a hydrocarbon-substituted mono primary ether amine, (ii) a dibasic acid anhydride, and (iii) an N-alkyl alkylene diamine.

Co-assigned U.S. 4,581,040 (Sung et al.) teaches the use of a reaction product as a deposit inhibitor additive in fuel compositions. The reaction product taught is a condensate product of the process comprising: (i) reacting a dibasic acid anhydride with a polyoxyisopropylenediamine thereby forming a maleamic acid; (ii) reacting the maleamic acid with a polyalkylene polyamine, thereby forming a condensate product; and (iii) recovering the condensate product.

Co-assigned U.S. 4,659,336 (Sung et al.) discloses the use of the mixture of: (i) the reaction product of maleic anhydride, a polyether polyamine containing oxyethylene and oxypropylene ether moieties, and a hydrocarbyl polyamine; and (ii) a polyolefin polymer/copolymer as an additive in motor fuel compositions to reduce engine ORI.

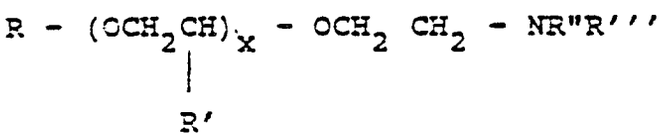
Co-assigned U.S. 4,659,337 (Sung et al.) discloses the use of the reaction product of maleic anhydride, a polyether polyamine containing oxyethylene and oxypropylene ether moieties, and a hydrocarbyl polyamine in a gasoline motor fuel to reduce engine ORI and provide carburetor detergency.

Co-assigned U. S. 4,643,738 (Sung et al.) discloses a motor fuel additive useful in reducing combustion chamber deposits, the additive prepared by reacting a dibasic acid anhydride, a polyoxyisopropylene diamine, and an N-alkyl-alkylene diamine.

Co-assigned U. S. 4,643,737 (Sung et al.) discloses a motor fuel additive useful in reducing combustion chamber deposits, the additive prepared by reacting maleic anhydride, an alpha-hydroxy omega-hydroxy-poly(oxyethylene) poly(oxypropylene) poly(oxyethylene) block copolymer, and an N-alkyl-alkylene diamine.

Co-assigned U. S. 4,631,069 (Sung) discloses a wear-inhibiting additive for use in alcohol fuel compositions, the additive prepared by reacting a polyoxyisopropylene diamine, a dibasic acid anhydride, and an N-alkyl-alkylene diamine.

U.S. 4,604,103 (Campbell) discloses a motor fuel deposit control additive for use in internal combustion engines which maintains cleanliness of the engine intake system without contributing to combustion chamber deposits or engine octane requirement increase (ORI). The additive disclosed is a hydrocarbyl polyoxyalkylene polyamine ethane of molecular weight range 300-2500 having the formula



where R is a hydrocarbyl radical of from 1 to about 30 carbon atoms; R' is selected from methyl and ethyl; x is an integer from 5 to 30; and R'' and R''' are independently selected from hydrogen and $-(CH_2CH_2NH-)_y H$ where y is an integer from 0-5.

U. S. 4,357,148 (Graiff) discloses a motor fuel additive useful in controlling ORI which is the combination of (a) an oil-soluble aliphatic polyamine containing at least one olefinic polymer chain, and (b) a polymer, copolymer, or corresponding hydrogenated polymer or copolymer of a C_2-C_6 mono olefin with a molecular weight of 500-1500.

U. S. 4,166,726 (Harle) discloses a fuel additive which is the combination of (i) the reaction product of an alkylphenol, an aldehyde, and an amine, and (ii) a polyalkylene amine.

U. S. 3,960,515 (Honnen) and U. S. 3,898,056 (Honnen) disclose the use of a mixture of high and low molecular weight hydrocarbyl amines as a detergent and dispersant in motor fuel compositions.

U. S. 3,438,757 (Honnen et al.) discloses the use of hydrocarbyl amines and polyamines with a molecular weight range of 450-10,000, alone or in combination with a lubricating mineral oil, as a detergent for motor fuel compositions.

It is one object of this invention to provide a gasoline-soluble reaction product additive for use in motor fuel compositions. It is another object of this invention to provide a concentrate composition comprising the reaction product additive dissolved in a hydrocarbon solvent. It is yet another object of this invention to provide a haze-free, deposit-resistant and ORI-inhibited motor fuel composition comprising the reaction product as well as a hydrocarbon solvent based concentrate composition which may be added to motor fuel to produce such a motor fuel composition.

It is one advantage of this invention that motor fuel compositions of the instant invention are haze-free, ORI-inhibited, and deposit-resistant. It is another advantage of this invention that the reaction product additive of the instant invention is soluble in gasoline and similar motor fuel compositions, and therefore requires no admixing with a solvent prior to introduction into a base motor fuel composition.

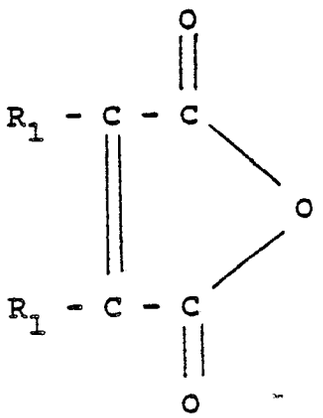
The invention will now be described by reference to two embodiments. The first embodiment is a soluble additive in a motor fuel composition and has utility as an ORI inhibitor. The second embodiment

provides a motor fuel composition exhibiting both reduced ORI and increased resistance to carburetor intake valve, intake manifold, and EGR system deposit formation in comparison with conventional motor fuel compositions.

FIRST EMBODIMENT OF THE INVENTION

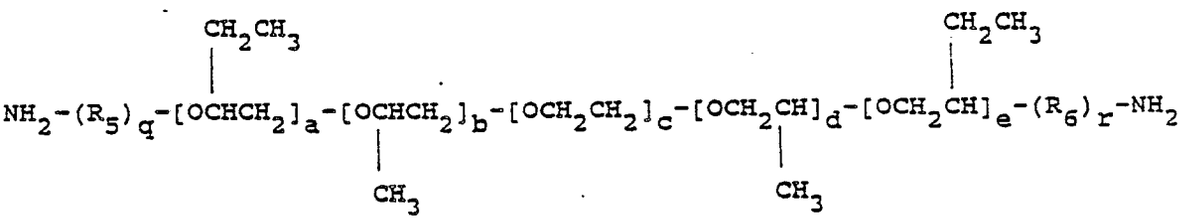
It has been discovered that a composition comprising the reaction product of a dibasic acid anhydride, a novel diamine containing block copolymers with polyalkylene backbones, and a hydrocarbyl polyamine has utility as an ORI inhibitor when employed as a soluble additive in a motor fuel composition. The novel reaction product of the instant invention is obtained by reacting at a temperature of 30° C-200° C, preferably 90° C-150° C:

(a) about 1 mole of a dibasic acid anhydride of the formula



where R_1 is either H or a C_1-C_5 alkyl radical, preferably H;

(b) 1-2 moles, preferably 1.5 moles of a polyoxyalkylene diamine of the formula



where R_5 and R_6 are C_1-C_{12} alkylene groups, preferably C_2-C_6 alkylene groups, q and r are integers having a value of 0 or 1, preferably with q = 1 and r = 0, c has a value from about 5-150, preferably 8-50, b + d has a value from about 5-150, preferably 8-50, and a + e has a value from about 2-12, preferably 4-8; and

(c) 1-2 moles, preferably 1 mole of a hydrocarbyl polyamine which may be either:

(i) a hydrocarbyl polyamine of the formula

$$R_2(NH\text{-}R_3)_x\text{ - }NH_2$$

where R_2 is a alkyl radical having from about 1-24, preferably about 12-20 carbon atoms, R_3 is an alkylene radical having from about 1-6 carbon atoms, and x has a value from about 1-10, preferably 1-5; or

(ii) a n-alkyl-alkylene diamine of the formula

$$R_4\text{-}NH\text{-}(CH_2)_n\text{-}NH_2$$

where R_4 is an aliphatic hydrocarbon radical having from about 1-24, preferably 12-20 carbon atoms and n

has a value from about 1-6, preferably having a value of 3.

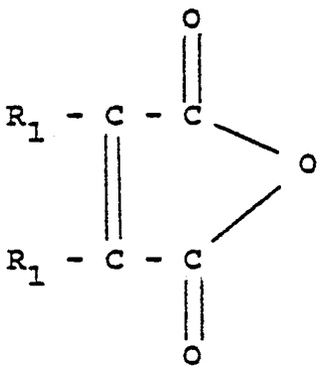
The instant invention is also directed to a concentrate comprising 1.0-75.0 weight percent, preferably 5.0-35.0 weight percent of the prescribed reaction product dissolved in a hydrocarbon solvent, preferably xylene. In addition, the instant invention is directed to a haze-free motor fuel composition comprising 0.0005-5.0 weight percent, preferably 0.001-1.0, most preferably 0.01-0.1 weight percent of the prescribed reaction product. An additional polymer/copolymer additive with a molecular weight range of 500-3500, preferably 650-2600 may also be employed in admixture with the motor fuel composition of the instant invention in concentrations of 0.001-1.0 wt. %, preferably 0.01-0.5 wt. %.

Referring now to the drawings, Figure 1 is a graphical representation of data obtained which compares the octane requirement (as a function of hours of engine operation) of a 1983 Chevrolet 2.0 liter engine using an unleaded base fuel containing 60 PTB of a commercial fuel additive, and the identical engine using a motor fuel composition of the instant invention which is an unleaded base fuel containing 100 PTB of the reaction product of the instant invention, as exemplified by Example II.

Figure 2 is a graphical representation of data obtained which compares the octane requirement (as a function of hours of engine operation) of a 1983 Chevrolet 2.0 liter engine using an unleaded base fuel containing 60 PTB of a commercial fuel additive, and the identical engine using a motor fuel composition of the instant invention, as exemplified by Example VI, which is an unleaded base fuel containing 30 PTB of the reaction product of the instant invention, as exemplified by Example II, in combination with 150 PTB of polyisobutylene of a molecular weight of about 1300.

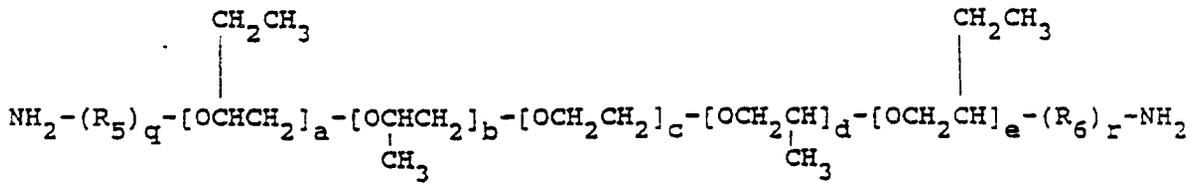
The reaction product additive of the instant invention is prepared by reacting a dibasic acid anhydride, a diamine containing block copolymers with polyoxyalkylene backbones and a hydrocarbyl polyamine.

The dibasic acid anhydride reactant used to prepare the reaction product is of the formula

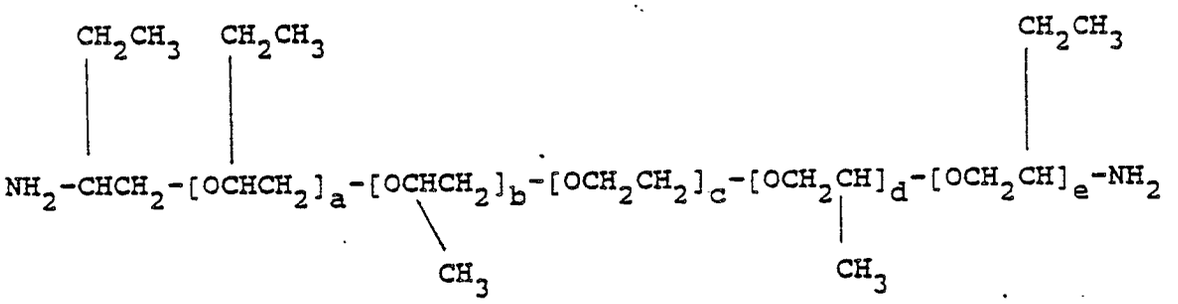


where R_1 is either H or a C_1-C_5 alkyl radical. Accordingly, dibasic acid anhydrides suitable for use include maleic anhydride; alpha-methyl maleic anhydride; alpha-ethyl maleic anhydride; and alpha, beta-dimethyl maleic anhydride. The preferred dibasic acid anhydride for use is maleic anhydride.

The polyoxyalkylene diamine reactant used to prepare the reaction product is a diamine of the formula



where R_5 and R_6 are C_1-C_{12} alkylene groups, preferably C_2-C_6 alkylene groups, most preferably a propylene or butylene group, q and r are integers having a value of 0 or 1, preferably with q-1 and r = 0, c has a value from about 5-150, preferably 8-50, b + d has a value from about 5-150, preferably 8-50, and a + e has a value from about 2-12, preferably 4-8. The novelty of the prescribed polyoxyalkylene diamine reactant resides in the fact that it contains a large number (5-150, preferably 8-50) of polyoxypropylene ether moieties in combination with a smaller number (2-12, preferably 4-8) of polyoxybutylene ether moieties. In the most preferred embodiment, q = 1, r = 0, R_5 is a butylene group, and the polyoxyalkylene diamine reactant is thereof of the formula



where c has a value of 8-50, b + d has a value of 8-50, and a + c has a value of 2-12.

The method of synthesis of the prescribed polyoxyalkylene diamine reactant is set forth in detail in co-assigned U. S. Pat. Appl. Ser. No. 000,253, and incorporated herein by reference. The best mode of synthesizing the preferred polyoxyalkylene diamine reactant is set forth in Example I, below.

Example I

Synthesis of Novel Polyoxyalkylene Diamine Reactant

A. Preparation of Polyol Precursor

Ten pounds of a polyethylene glycol of an approximate molecular weight of 600 and 100 g of 45% aqueous KOH were charged into a ten-gallon reactor, which was then purged with prepurified nitrogen. While maintaining a nitrogen purge, the reactor was heated to 100 °C, and the initiator was then dried to a water content of less than 0.1% by vacuum stripping followed by nitrogen stripping. Thereafter, 19.1 lb of ethylene oxide was charged and reacted at 105-110 °C and 50 psig for 1.25 hours. Without digestion, 26.2 lb of propylene oxide was then charged and reacted at 105-110 °C and 50 psig over a 3 hour period.

The reaction mixture was thereafter heated to about 120 °C, and 2.9 lb. of butylene oxide was added over a 30 minute period. After a 2 hour digestion period, the alkaline polyol was neutralized by stirring for 2 hours with 360 g of MAGNESOL 30/40, which was added as an aqueous slurry. To stabilize the material, 26.4 g of di-t-butyl p-cresol was added. The neutralized product was then vacuum stripped to about 5 mm Hg pressure, nitrogen stripped, and filtered. The finished product had the following properties:

Acid no., mg KOH/g	0.01
Hydroxyl no., mg KOH/g	35
Water, wt %	0.01
pH in 10:6 isopropanol-water	8.1
Color, Pt-Co	40
Sodium, ppm	0.2
Potassium, ppm	0.2
Peroxide, ppm	1.1
Viscosity, °F, cc 77	988
100	513

B. Amination Reaction

0.6 lb/hr of the polyol, 1.2 lb/hr of ammonia, and 36 liter/hr of hydrogen were fed into a 1250 ml tubular reactor filled with a nickel-chromium-copper metal and metal oxide catalyst which was kept at 200° C and 2000 psig. The reactor effluent was stripped at 100° C and 10mm Hg vacuum. The resulting polyether polyamine product had the following physical properties:

Total acetylatables, meq/g	0.615
Total amine, meq/g	0.56
Primary amine, meq/g	0.54
Water, wt%	0.09
Color, Pt-Co	30
Flash Point, PMCC	440° F
Melting point, ° C	27-31

The hydrocarbyl polyamine reactant used to prepare the reaction product may be either:
(i) a hydrocarbyl polyamine of the formula

$R_2(NH\text{-}R_3)_x\text{-}NH_2$

where R_2 is an alkyl radical having from about 1-24, preferably 12-20 carbon atoms, R_3 is an alkylene radical having from about 1-6 carbon atoms, and x has a value from 1-10, preferably 1-5;
or
(ii) a n-alkyl-alkylene diamine of the formula

$R_4 - NH - (CH_2)_n - NH_2$

where R_4 is an aliphatic hydrocarbon radical having from about 1 to 24 carbon atoms, preferably from about 12 to 20 carbon atoms, and n has a value from about 1 to 6, preferably having a value of 3. N-alkyl-alkylene diamines suitable for use in preparing the reaction product of the instant invention include aliphatic diamines commercially available from Akzo Chemie America Co. under the DUOMEEN series trade name. Examples of such n-alkyl-alkylene diamines include n-coco-1,3-diaminopropane (DUOMEEN C), n-soya-1,3-diaminopropane (DUOMEEN S), n-tallow-1,3-diaminopropane (DUOMEEN T), and n-oleyl-1,3-diaminopropane (DUOMEEN OL). The most preferred n-alkyl-alkylene diamine reactant for use in preparing the reaction product is n-tallow-1,3 diaminopropane.

The reaction product is prepared by first reacting about 1 mole of dibasic acid anhydride with about 1 to 2 moles, preferably 1.5 moles of the prescribed novel diamine containing block copolymers with polyoxyethylene, polyoxypropylene and polyoxybutylene backbones at a temperature of 30° C-200° C, preferably 90° C-150° C. The reaction of dibasic acid anhydride with the novel polyoxyalkylene diamine is preferably carried out in the presence of a solvent. A preferred solvent is one which will distill with water azeotropically. Suitable solvents include hydrocarbons boiling in the gasoline boiling range of about 30° C to about 200° C. Generally, this will include saturated and unsaturated hydrocarbons having from about 5 to about 10 carbon atoms. Specific suitable hydrocarbon solvents include hexane, cyclohexane, benzene, toluene, and mixtures thereof. Xylene is the preferred solvent. The solvent can be present in an amount of up to about 90% by weight of the total reaction mixture. The reaction mixture is thereafter cooled to 50° C-75° C, preferably 60° C, and 1-2 moles, preferably 1 mole of the hydrocarbyl polyamine is added. The new mixture is then reacted at 30° C-200° C, preferably 90° C-150° C.

In the best mode of preparing the reaction product of the instant invention, about 1 mole of maleic anhydride and about 1.5 moles of the prescribed polyoxyalkylene diamine where c has a value of 8-50, b + d has a value of 8-50, and a + e has a value of 4-8 are combined with the solvent xylene and reacted at a temperature of about 100° C. The reaction is maintained at this temperature for approximately 2 hours. The mixture is then cooled to about 60° C, whereupon about 1 mole of the hydrocarbyl polyamine n-tallow-1,3 diaminopropane is added. The new mixture is then reacted at about 140° C for reflux and azeotroping for 5 hours, with about 1 to 1.5 moles of water being removed. The reaction product can then be separated from the solvent using conventional means, or left in admixture with some or all of the solvent.

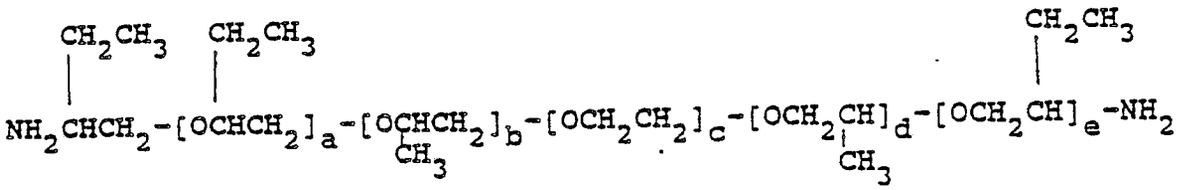
A critical feature of the reaction product composition of the instant invention is the presence of a large number (5-150, preferably 8-50) of polyoxypropylene ether moieties in combination with more limited numbers (2-12, preferably 4-8) of polyoxybutylene ether moieties. These moieties are provided by the prescribed novel polyoxyalkylene diamine reactant. In particular, the presence of a large number of

polyoxypropylene ether moieties enhances the gasoline solubility of the reaction product, thus increasing the efficacy of the reaction product as an additive in motor fuel compositions. The reaction product additive of the instant invention is advantageous over other ORI-controlling motor fuel additives such as those disclosed in U. S. Pat. Appl. Serial Nos. 845,719 and 821,727, in that the reaction product of the instant invention is soluble in gasoline and similar motor fuel compositions, and therefore requires no admixing with a solvent prior to introduction into a base motor fuel composition. In addition, the presence of polyoxybutylene ether moieties in the reaction product of the instant invention has been found to prevent hazing in a motor fuel composition of the instant invention.

The following examples illustrate the preferred method of preparing the novel reaction product of the instant invention. It will be understood that the following examples are merely illustrative, and are not meant to limit the invention in any way. In the examples, all parts are parts by weight unless otherwise specified.

Example II

A reaction product was formed by reacting 54 parts of maleic anhydride, 3265 parts of xylene, and 3000 parts of a polyoxyalkylene diamine at 100° C for 2 hours. The polyoxyalkylene diamine was of the formula

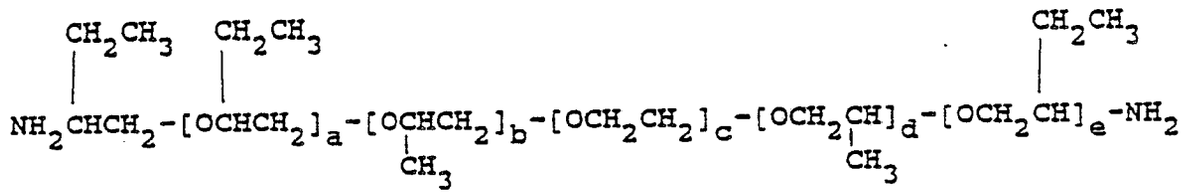


where c had an approximate value of 40.5, b+d had an approximate value of 40.5, and a+e had an approximate value of 2.5.

The mixture was thereafter cooled to about 60° C, and 54 parts of n-tallow-1,3 diaminopropane (DUOMEEN T) were added. The new mixture was then reacted at about 140° C for 5 hours to produce the final reaction product. The final reaction product was then filtered and stripped of remaining solvent under vacuum.

Example III

A reaction product is formed by reacting 54 parts of maleic anhydride, 3206 parts of xylene, and 3000 parts of a polyoxyalkylene diamine at 100° C for 2 hours. The polyoxyalkylene diamine is of the formula

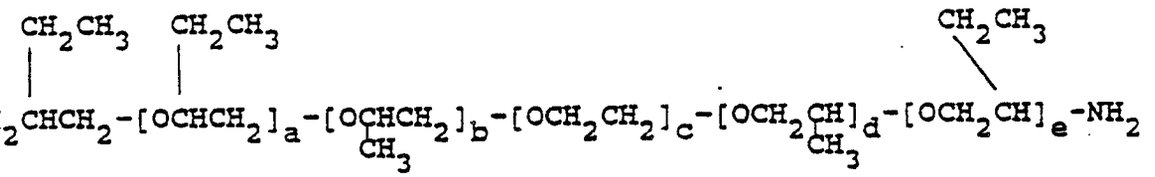


where c has an approximate value of 40.5, b+d has an approximate value of 40.5, and a+e has an approximate value of 2.5.

The mixture is thereafter cooled to about 60° C, and 152 parts of n-coco-1,2 diaminopropane (DUOMEEN C) are added. The new mixture is then reacted at about 140° C for 5 hours to produce the final reaction product. The final reaction product is then filtered and stripped of remaining solvent under vacuum.

Example IV

A reaction product is formed by reacting 54 parts of maleic anhydride, 3231 parts of xylene, and 3000 parts of a polyoxyalkylene diamine at 100° C for 2 hours. The polyoxyalkylene diamine is of the formula



where c has an approximate value of 40.5, b+d has an approximate value of 40.5, and a+e has an approximate value of 2.5.

The mixture is thereafter cooled to about 60° C, and 176 parts of n-oleyl-1,3 diaminopropane (DUOMEEN OL) are added. The new mixture is then reacted at about 140° C for 5 hours to produce the final reaction product. The final reaction product is then filtered and stripped of remaining solvent under vacuum.

It has been found that a motor fuel composition containing 0.0005-5.0 weight percent, preferably 0.001-1.0 preferably 0.01-0.1 weight percent of the reaction product of the instant invention is surprisingly effective in minimizing and reducing the ORI of a gasoline internal combustion engine. This improvement has been demonstrated in engine tests where the performance characteristics of a base motor fuel composition containing a commercial fuel additive and an improved motor fuel composition of the instant invention were compared. The specific engine tests were made on a 2.0 liter 1983 Chevrolet four cylinder engine (Chevy Test). This test correlates well with results obtained via road simulation tests.

The base motor fuel employed in the tests (herein designated as Base Fuel A) was a premium grade gasoline essentially unleaded (less than 0.05 g of tetraethyl lead per gallon), and comprised a mixture of hydrocarbons boiling in the gasoline boiling range consisting of about 22% aromatic hydrocarbons, 11% olefinic carbons, and 67% paraffinic hydrocarbons, boiling in the range from about 90° F to 450° F. In preparing motor fuels for the Chevy Test, a suitable amount of the reaction product of the instant invention was added directly to Base Fuel A without any hazing of the motor fuel composition, and without additional solvents being necessary. As previously stated, the gasoline solubility of the reaction product of the instant invention is attributed to the presence of a large number of polyoxypropylene ether moieties in combination with polyoxyethylene and polyoxybutylene ether moieties. The haze-free property of the motor fuel composition comprising the reaction product is attributed to the presence of the polyoxybutylene ether moieties.

The ORI tendencies of Base Fuel A containing 60 PTB of a commercial fuel additive (60 pounds of reaction product per 1000 barrels of gasoline, equivalent to about 0.02 weight percent of reaction product based on the weight of the fuel composition), as well as Base Fuel A containing 100 PTB of the reaction product of Example II (100 pounds of reaction product per 1000 barrels of gasoline, equivalent to about 0.033 weight percent of reaction product based upon the weight of the fuel composition) were measured using the Chevy Test. The Chevy Test employs a 2.0 liter 1983 Chevrolet in-line four cylinder engine with a cast alloy iron cylinder head having separate intake and exhaust ports for each cylinder. An electronically controlled fuel injection system maintains the required fuel flow to each engine cylinder by monitoring various engine operating parameters (e.g. manifold absolute pressure, throttle valve position, coolant temperature, engine r.p.m., and exhaust gas oxygen content) and adjusting the fuel flow accordingly. The fuel system supplying fuel to the engine is specifically adapted for the determination of engine ORI. At the beginning of the engine rating procedure, a fuel with an octane rating high enough to ensure that no audible engine knock is present is employed. The next lower octane fuel is then switched with the previous fuel, and this procedure continues until a knock becomes audible. The difference between the octane level at knock and no-knock conditions is the engine ORI. Engine ORI was determined as a function of hours of engine operation for both Base Fuel A containing 100 PTB of reaction product, and for Base Fuel A containing 60 PTB of a typical commercial motor fuel additive.

The experimental results obtained from the Chevy Test for Base Fuel A containing 60 PTB of commercial fuel additive and Base Fuel A containing 100 PTB of the reaction product of the instant invention (Example II) are set forth in Figure 1. As illustrated by Figure 1, the octane requirement of the engine using Base Fuel A containing 60 PTB of commercial fuel additive was consistently higher than the

corresponding octane requirement of the engine using Base Fuel A containing 100 PTB of Example II over the duration of the test. The data set forth in Figure 1 thus indicate that the reaction product of the instant invention is more effective as an ORI controlling additive in a motor fuel composition than a typical commercially available motor fuel composition.

The motor fuel composition of the instant invention comprises a major amount of a base motor fuel and 0.0005-5.0 weight percent, preferably 0.001-1.0, most preferably 0.01-0.1 weight percent of the above-described reaction product. Preferred base motor fuel compositions for use with the reaction product additive are those intended for use in spark ignition internal combustion engines. Such motor fuel compositions, generally referred to as gasoline base stocks, preferably comprise a mixture of hydrocarbons boiling in the gasoline boiling range, preferably from about 90°F to about 450°F. This base fuel may consist of straight chains or branched chains or paraffins, cycloparaffins, olefins, aromatic hydrocarbons, or mixtures thereof. The base fuel can be derived from, among others, straight run naphtha, polymer gasoline, natural gasoline, or from catalytically cracked or thermally cracked hydrocarbons and catalytically reformed stock. The composition and octane level of the base fuel are not critical and any conventional motor fuel base can be employed in the practice of this invention. In addition, the motor fuel composition may contain any of the additive generally employed in gasoline. Thus, the fuel composition can contain anti-knock compounds such as tetraethyl lead compounds, anti-icing additives, upper cylinder lubricating oils, and the like.

The motor fuel composition of the instant invention may additionally comprise a polymeric component, present in a concentration ranging from about 0.001-1.0 weight percent, preferably 0.01-0.5 weight percent, based on the total weight of the motor fuel composition. The polymeric component may be a polyolefin polymer, copolymer, or corresponding hydrogenated polymer or copolymer of a C_2-C_6 unsaturated hydrocarbon. The polymer component is prepared from monoolefins and diolefins, or copolymers thereof, having an average molecular weight in the range from abut 500-3500, preferably about 650-2600. Mixtures of olefin polymers with an average molecular weight falling within the foregoing range are also effective. In general, the olefin monomers from which the polyolefin polymer component is prepared are unsaturated C_2-C_6 hydrocarbons. Specific olefins which may be employed to prepare the polyolefin polymer component include ethylene, propylene, isopropylene, butylene, isobutylene, amylene, hexylene, butadiene, and isoprene. Propylene, isopropylene, butylene, and isobutylene are particularly preferred for use in preparing the polyolefin polymer component. Other polyolfins which may be employed are those prepared by cracking polyolefin polymers or copolymers of high molecular weight to a polymer in the above-noted molecular weight range. Derivatives of the noted polymers obtained by saturating the polymers by hydrogenation are also effective and are a part of this invention. The word "polymers" is intended to include the polyolefin polymers and their corresponding hydrogenated derivatives.

The average molecular weight range of the polymer component is a critical feature. The polyolefin polymer, copolymer, or corresponding hydrogenated polymer or copolymer component may have an average molecular weight in the range from abut 500-3500, preferably from about 650-2600. The most preferred polymer components for use in the instant invention are polypropylene with an average molecular weight in the range of about 750-1000, preferably about 800, and polyisobutylene with an average molecular weight in the range of about 1000-1500, preferably about 1300. The polymer component, if employed, enhances the ORI reduction of the instant invention, and additionally provides enhanced cleanliness at the engine intake valves and ports.

Examples V and VI, set forth below, are illustrative of motor fuel compositions of the instant invention comprising the above-described reaction product and polymer components. It will be understood that the following examples are merely illustrative, and are not meant to limit the invention in any way.

Example V

A motor fuel composition was obtained by mixing with Base Fuel A about 100 PTB of the reaction product component set forth in Example II (equivalent to about 0.033 wt. %) and about 150 PTB of polypropylene polymer component of a molecular weight of about 800 (equivalent to about 0.05 wt. %).

Example VI

A motor fuel composition was obtained by mixing with Base Fuel A about 30 PTB of the reaction product component set forth in Example II (equivalent to about 0.01 wt. %) and about 150 PTB of polyisobutylene of a molecular weight of about 1300 (equivalent to about 0.05 wt. %).

Chevy Test data comparing ORI for Base Fuel A containing 60 PTB of commercial fuel additive and a motor fuel composition of the instant invention (Example VI), which is Base Fuel A containing 30 PTB of the reaction product of Example II combined with 150 PTB of polyisobutylene of a molecular weight of about 1300 are set forth in Figure 2. As illustrated by Figure 2, the octane requirement of the engine using Base Fuel A containing 60 PTB of commercial fuel additive was consistently higher than the corresponding octane requirement of the engine using a motor fuel composition of the instant invention over the duration of the test. The data set forth in Figure 2 thus indicate that the reaction product of the instant invention, in admixture with the prescribed optional polymer component, is more effective as an ORI controlling additive in a motor fuel composition than a typical commercially available motor fuel composition.

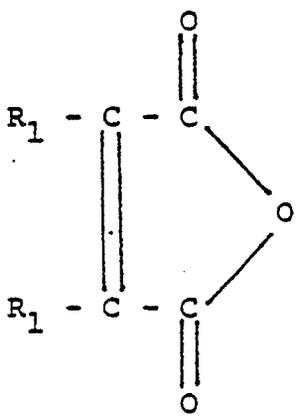
For convenience in shipping and handling, it is useful to prepare a concentrate of the reaction product additive which may be added to a base motor fuel to produce the motor fuel composition of the instant invention. The concentrate may be prepared in a suitable liquid solvent containing from about 1.0-75.0 weight percent, preferably 5.0-35.0 weight percent of the additive component or components: namely, the above-described novel reaction product either alone or in combination with the above-described additional polymer component. Suitable solvents for use in the concentrate include hydrocarbon solvents such as toluene and xylene, with xylene being preferred.

SECOND EMBODIMENT OF THE INVENTION

Motor fuel compositions of the instant invention show improved ORI-inhibition and carburetor and valve deposit resistance over conventional motor fuel compositions. Motor fuel compositions of the instant invention comprise a mixture of hydrocarbons boiling in the range 90°F-450°F and additionally comprise:

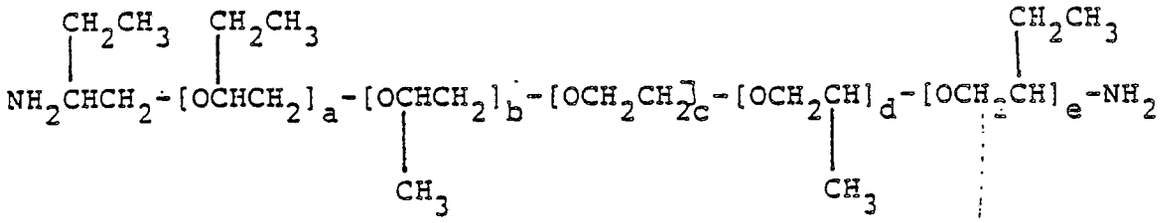
(I) from 0.0005-5.0 weight percent of the reaction product obtained by reacting a temperature of 30°C-200°C:

(a) about 1 mole of a dibasic acid anhydride of the formula



where R_1 is H or a C_1-C_5 alkyl radical,

(b) 1-2 moles of a polyoxyalkylene diamine of the formula



where c has a value from about 5-150, b + d has a value from about 5-150, and a + e has a value from about 2-12, and

(c) 1-2 moles of a hydrocarbyl polyamine which may be either

(i) a hydrocarbyl polyamine of the formula

$R_2(NH\text{-}R_3)_x \text{ - } NH_2$

where R_2 is an alkyl radical having from about 1-24 carbon atoms, R_3 is an alkylene radical having from about 1-6 carbon atoms, and x has a value from about 1-10, or

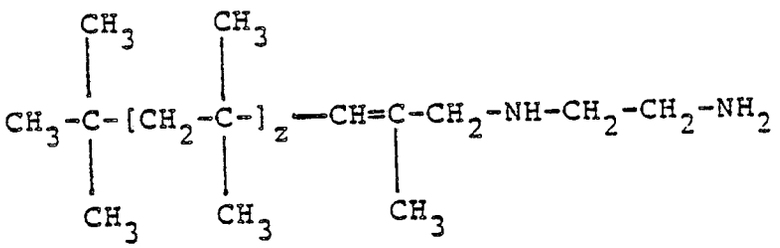
(ii) a n-alkyl-alkylene diamine of the formula

$R_4\text{-}NH\text{-}(CH_2)_n\text{-}NH_2$

where R_4 is an aliphatic hydrocarbon radical having from about 1-24 carbon atoms and n has a value from about 1-6; and

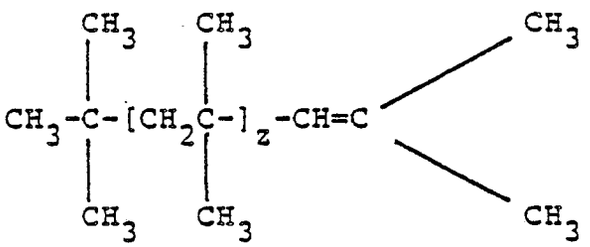
(II) from 0.001-1.0 weight percent of a mixture comprising a hydrocarbon solvent and:

(a) 50-75 parts by weight of polyisobutylene ethylene diamine of the formula



and

(b) 5-25 parts by weight of polyisobutylene of the formula



where z has a value of 30-40.

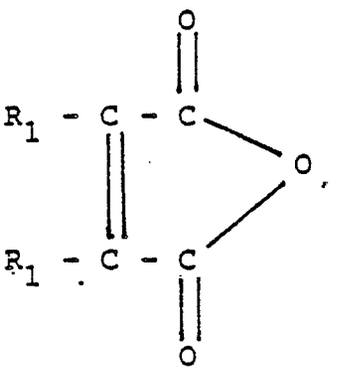
The instant invention is also directed to a concentrate comprising a hydrocarbon solvent in admixture with 0.1-10.0 weight percent of the abovedescribed reaction product component and 25.0-75.0 weight percent of the abovedescribed hydrocarbon solvent-polyisobutylene ethylene diamine-polyisobutylene mixture.

Referring now to the drawings, Figure 3 is a graphical representation of data obtained which compares the octane requirement (as a function of hours of engine operation) of a Chevrolet 1.8 liter engine using an commercial unleaded base fuel containing 60 PTB of a commercial fuel additive, and the identical engine using a motor fuel composition of the instant invention as exemplified by Example IV. Figure 4 is a

graphical representation of data obtained which compares the octane requirement (as a function of hours of engine operation) of a Chevrolet 2.0 liter engine using a commercial gasoline, and the identical engine using a motor fuel composition of the instant invention as exemplified by Example IV.

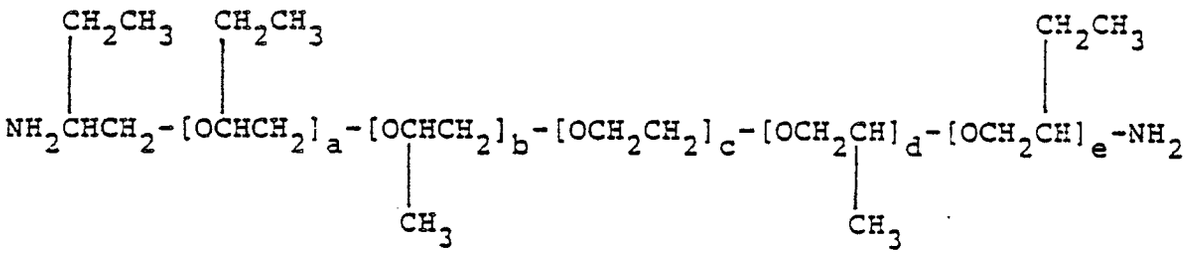
Component (I) of the instant invention is a reaction product prepared by reacting a dibasic acid anhydride, a diamine containing block copolymers with polyoxyalkylene backbones, and a hydrocarbyl polyamine. The reaction product component of the instant invention is identical to the reaction product disclosed in co-assigned U. S. Pat. Appl. Serial No. 000,230 (D#78,679), incorporated herein by reference.

The dibasic acid anhydride reactant used to prepare the reaction product component of the instant invention is of the formula



where R_1 is either H or a C_1-C_5 alkyl radical. Accordingly, dibasic acid anhydrides suitable for use include maleic anhydride; alpha-methyl maleic anhydride; alpha-ethyl maleic anhydride; and alpha, beta-dimethyl maleic anhydride. The preferred dibasic acid anhydride for use is maleic anhydride.

The polyoxyalkylene diamine reactant used to prepare the reaction product component of the instant invention is a diamine of the formula



where c has a value from about 5-150, preferably 8-50; b + d has a value from about 5-150, preferably 8-50; and a + e has a value from about 2-12, preferably 4-8. The novelty of the prescribed polyoxyalkylene diamine reactant resides in the fact that it contains a large number (5-150, preferably 8-50) of polyoxypropylene and polyoxyethylene ether moieties in combination with a smaller number (2-12, preferably 4-8) of polyoxybutylene ether moieties. The method of synthesis of the prescribed novel polyoxyalkylene diamine reactant is set forth in detail in co-assigned U. S. Pat. Appl. Serial No. 000,253 (D#78,650), incorporated herein by reference.

The hydrocarbyl polyamine reactant used to prepare the reaction product component of the instant invention may be either:

(i) a hydrocarbyl polyamine of the formula

$R_2(NH\text{-}R_3)_x\text{-}NH_2$

where R_2 is an alkyl radical having from about 1-24, preferably 12-20 carbon atoms, R_3 is an alkylene radical having from about 1-6 carbon atoms, and x has a value from 1-10, preferably 1-5;

or

(ii) a n-alkyl-alkylene diamine of the formula

$R_4 - NH - (CH_2)_n - NH_2$

where R_4 is an aliphatic hydrocarbon radical having from about 1 to 24 carbon atoms, preferably from about 12 to 20 carbon atoms, and n has a value from about 1 to 6, preferably having a value of 3. N-alkyl-alkylene diamines suitable for use in preparing the reaction product of the instant invention include aliphatic diamines commercially available from Akzo Chemie America Co. under the DUOMEEN series trade name. Examples of such n-alkyl-alkylene diamines include n-coco-1,3-diaminopropane (DUOMEEN C), n-soya-1,3-diaminopropane (DUOMEEN S), n-tallow-1,3-diaminopropane (DUOMEEN T), and n-oleyl-1,3-diaminopropane (DUOMEEN OL). The most preferred n-alkyl-alkylene diamine reactant for use in preparing the reaction product component of the instant invention is n-tallow-1,3 diaminopropane.

The reaction product component of the instant invention is prepared by first reacting about 1 mole of dibasic acid anhydride with about 1 to 2 moles, preferably 1.5 moles of the prescribed diamine reactant containing block copolymers with polyoxyethylene, polyoxypropylene and polyoxybutylene backbones at a temperature of 30° C-200° C, preferably 90° C-150° C. The reaction of dibasic acid anhydride with the polyoxyalkylene diamine reactant is preferably carried out in the presence of a solvent. A preferred solvent is one which will distill with water azeotropically. Suitable solvents include hydrocarbons boiling in the gasoline boiling range of about 30° C to about 200° C. Generally, this will include saturated and unsaturated hydrocarbons having from about 5 to about 10 carbon atoms. Specific suitable hydrocarbon solvents include hexane, cyclohexane, benzene, toluene, and mixtures thereof. Xylene is the preferred solvent. The solvent can be present in an amount of up to about 90% by weight of the total reaction mixture. The reaction mixture is thereafter cooled to 50° C-75° C, preferably 60° C, and 1-2 moles, preferably 1 mole of the hydrocarbyl polyamine is added. The new mixture is then reacted at 30° C-200° C, preferably 90° C-150° C.

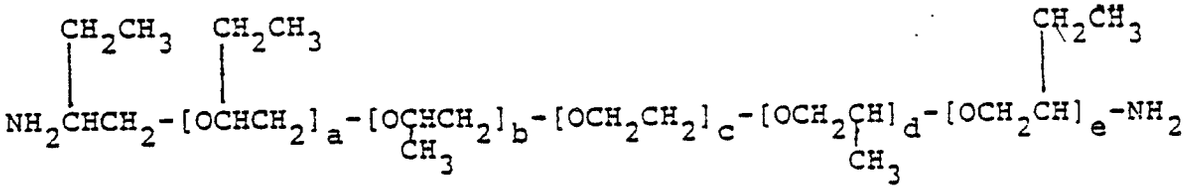
In a preferred mode of preparing the reaction product component of the instant invention, about 1 mole of maleic anhydride and about 1.5 moles of the prescribed polyoxyalkylene diamine where c has a value of 8-50, b+d has a value of 8-50, and a+e has a value of 4-8 are combined with the solvent xylene and reacted at a temperature of about 100° C. The reaction mixture is maintained at this temperature for approximately 2 hours. The mixture is then cooled to about 60° C, whereupon about 1 mole of the hydrocarbyl polyamine n-tallow-1,3 diaminopropane is added. The new mixture is then reacted at about 140° C for reflux and azeotroping for 5 hours, with about 1 to 1.5 moles of water being removed. The reaction product can then be separated from the solvent using conventional means, or left in admixture with some or all of the solvent.

A critical feature of the reaction product component of the instant invention is the presence of a large number (5-150, preferably 8-50) of polyoxypropylene and polyoxyethylene ether moieties in combination with more limited numbers (2-12, preferably 4-8) of polyoxybutylene ether moieties. These moieties are provided by the prescribed polyoxyalkylene diamine reactant. In particular, the presence of a large number of polyoxypropylene and polyoxyethylene ether moieties enhances the gasoline solubility of the reaction product component, thus increasing the efficacy of the reaction product as an additive in motor fuel compositions. The reaction product component of the instant invention is advantageous over other reaction product additives employed to control ORI in motor fuels such as those disclosed in co-assigned U. S. Patents 4,659,336 and 4,659,337 in that the reaction product component of the instant invention is soluble in gasoline and similar motor fuel compositions, and therefore requires no admixing with a solvent prior to introduction into a base motor fuel composition.

The following examples illustrate the preferred method of preparing the novel reaction product component of the instant invention. It will be understood that the following examples are merely illustrative, and are not meant to limit the invention in any way. In the examples, all parts are parts by weight unless otherwise specified.

Example I

In the best mode for preparing the reaction product component of the instant invention, 54 parts of maleic anhydride, 3265 parts of xylene, and 3000 parts of a polyoxyalkylene diamine were reacted at a temperature of 100° C for 2 hours. The polyoxyalkylene diamine was of the formula

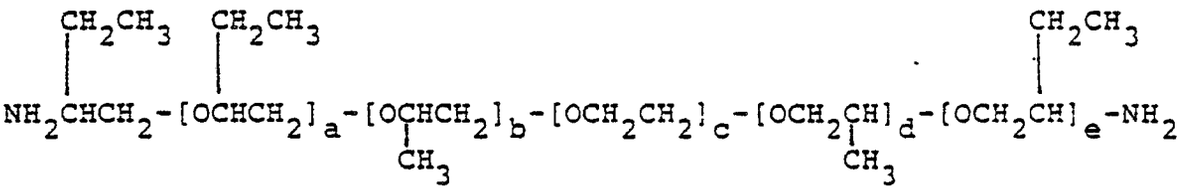


where c had an approximate value of 5-150, b + d had an approximate value of 5-150, and a + e had an approximate value of 2-12.

The mixture was thereafter cooled to about 60° C, and 54 parts of n-tallow-1,3 diaminopropane (DUOMEEN T) were added. The new mixture was then reacted at about 140° C for 5 hours to produce the final reaction product. The final reaction product was then filtered and stripped off remaining solvent under vacuum.

Example II

A reaction product is formed by reacting 54 parts of maleic anhydride, 3206 parts of xylene, and 3000 parts of a polyoxyalkylene diamine at 100° C for 2 hours. The polyoxyalkylene diamine is of the formula

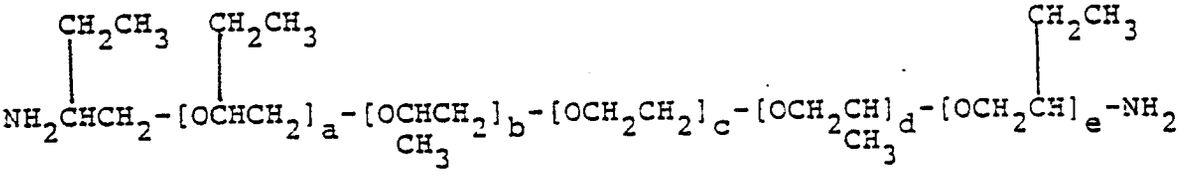


where c has an approximate value of 5-150, b + d has an approximate value of 5-150, and a + e has an approximate value of 2-12.

The mixture is thereafter cooled to about 60° C, and 152 parts of n-coco-1,2 diaminopropane (DUOMEEN C) are added. The new mixture is then reacted at about 140° C for 5 hours to produce the final reaction product. The final reaction product is then filtered and stripped of remaining solvent under vacuum.

Example III

A reaction product is formed by reacting 54 parts of maleic anhydride, 3231 parts of xylene, and 3000 parts of a polyoxyalkylene diamine at 100° C for 2 hours. The polyoxyalkylene diamine is of the formula



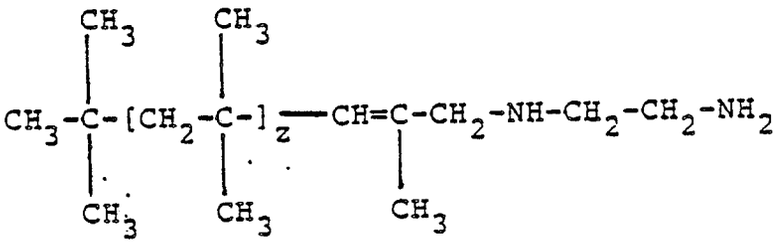
where c has an approximate value of 5-150, b + d has an approximate value of 5-150, and a + e has an approximate value of 2-12.

The mixture of thereafter cooled to about 60° C, and 176 parts of n-oleyl-1,3 diaminopropane (DUOMEEN OL) are added. The new mixture is then reacted at about 140° C for 5 hours to produce the final reaction product. The final reaction product is then filtered and stripped of remaining solvent under vacuum.

Component (II) of the motor fuel composition of the instant invention is a mixture of a major amount of polyisobutylene ethylene diamine and a minor amount of polyisobutylene. These subcomponents will

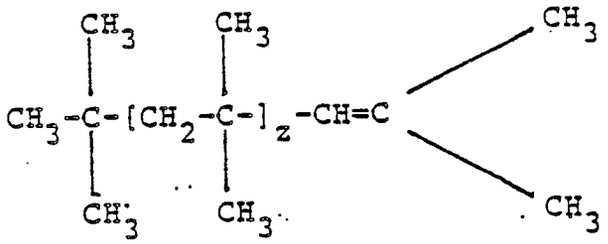
usually be employed in admixture with a hydrocarbon solvent to facilitate addition of Component (II) to a base motor fuel composition.

The polyisobutylene ethylene diamine subcomponent of Component (II) of the instant invention is typically present in a concentration range of 50-75 parts, preferably about 60 parts by weight, based upon the weight of the entire composition which makes up Component (II). The polyisobutylene ethylene diamine subcomponent is of the formula



where z has a value of 30-40, preferably 32-35, most preferably 33.

The polyisobutylene subcomponent of Component (II) of the instant invention is typically present in a concentration range of 5-25 parts, preferably 10-20 parts by weight, based upon the weight of the entire composition which makes up Component (II). The polyisobutylene subcomponent is of the formula



where z again has a value of 30-40, preferably 32-35, most preferably 33.

The hydrocarbon solvent employed to facilitate admixture of the abovedescribed subcomponents is preferably a light aromatic distillate composition. A commercially available light aromatic distillate composition containing the abovedescribed polyisobutylene ethylene diamine and polyisobutylene compounds in the abovespecified concentrations and particularly preferred for use as Component (II) of the instant invention is the commercial gasoline additive ORONITE OGA-472, available from Chevron Chemical Company. ORONITE OGA-472 is a composition containing approximately 60 parts by weight of polyisobutylene ethylene diamine, approximately 13 parts by weight polyisobutylene, and approximately 27 parts by weight light aromatic distillate, including xylene and C_9 alkylbenzenes. Fuel compositions containing ORONITE OGA-472 as an additive include those described in U. S. 4,141,693 (Feldman et al.), 4,028,065 (Sprague et al.), and 3,966,429 (Sprague et al.).

The motor fuel composition of the instant invention comprises a major amount of a base motor fuel and 0.0005-5.0 weight percent, preferably 0.001-1.0 weight percent of Component (I) (the abovedescribed reaction product component) and 0.001-1.0 weight percent, preferably 0.01-0.5 weight percent of Component (II), (the abovedescribed mixture comprising a major amount of polyisobutylene ethylene diamine and a minor amount of polyisobutylene in a hydrocarbon solvent). Preferred base motor fuel compositions are those intended for use in spark ignition internal combustion engines. Such motor fuel compositions, generally referred to as gasoline base stocks, preferably comprise a mixture of hydrocarbons boiling in the gasoline boiling range, preferably from about 90° F to about 450° F. This base fuel may consist of straight chains or branched chains or paraffins, cycloparaffins, olefins, aromatic hydrocarbons, or mixtures thereof. The base fuel can be derived from, among others, straight run naphtha, polymer gasoline, natural gasoline, or from catalytically cracked or thermally cracked hydrocarbons and catalytically reformed stock. The composition and octane level of the base fuel are not critical and any conventional motor fuel base can be employed in the practice of this invention. In addition, the motor fuel composition may contain any of the additives generally employed in gasoline. Thus, the fuel composition can contain conventional carburetor detergents, anti-knock compounds such as tetraethyl lead compounds, anti-icing additives, upper cylinder lubricating oils, and the like. A motor fuel composition representing the best mode of practicing the instant

invention is set forth in Example IV, below.

Example IV

In the best mode of practicing the instant invention, 30 PTB of the reaction product set forth in Example I (i.e. 30 pounds of reaction product per 1000 barrels of gasoline, equivalent to about 0.01 weight percent of reaction product component based on the weight of the fuel composition) and 205 PTB (about 0.07 weight percent) of a composition (ORONITE 0GA-472) containing approximately 60 parts by weight polyisobutylene ethylene diamine, approximately 13 parts by weight polyisobutylene, and approximately 27 parts by weight light aromatic distillate comprising xylene and C_9 alkylbenzenes were added to a major amount of a base motor fuel composition which comprises a mixture of hydrocarbons boiling in the range of about 90° F-450° F.

It has been found that a motor fuel composition containing 0.0005-5.0 weight percent, preferably 0.001-1.0 weight percent of Component (I) and 0.001-1.0 weight percent, preferably 0.01-0.5 weight percent of Component (II) is effective in both minimizing and reducing the ORI of a gasoline internal combustion engine, and in improving carburetor detergency and intake valve cleanliness of the motor fuel. These improvements have been demonstrated in ORI and carburetor detergency tests where the performance characteristics of a base motor fuel composition containing a commercial fuel additive and an improved motor fuel composition of the instant invention were compared.

The base motor fuel employed in the tests (herein designated as Base Fuel A) was a premium grade gasoline essentially unleaded (less than 0.05 g of tetraethyl lead per gallon), and comprised a mixture of hydrocarbons boiling in the gasoline boiling range consisting of about 22% aromatic hydrocarbons, 11% olefinic carbons, and 67% paraffinic hydrocarbons, boiling in the range from about 90° F to 450° F. In preparing motor fuels for the ORI and carburetor, intake valve and manifold detergency tests, a suitable amount of the reaction product component of the instant invention was added directly to Base Fuel A without additional solvents being necessary. As previously stated, the gasoline solubility of the reaction product component of the instant invention is attributed to the presence of a large number of polyoxypropylene ether moieties in combination with polyoxyethylene and polyoxybutylene ether moieties.

The ORI tendencies of Base Fuel A containing 60 PTB of a commercial fuel additive (60 pounds of reaction product per 1000 barrels of gasoline, equivalent to about 0.02 weight percent of reaction product based on the weight of the fuel composition), as well as a motor fuel composition of the instant invention, as exemplified by Example IV, were measured via the Fuel Related Deposit Test (FRDT). The test measures the octane requirement of an engine for a particular motor fuel as a function of varying engine speed and load. This test employs a 1.8 liter Chevrolet engine controlled by a dedicated computer which operates the engine speed and load controls, test stand safeties, and data acquisition. Due to the multifunctional capabilities of the computer controlled system, the test cycle very closely simulates an actual engine in a vehicle. The computer can change the engine speed and load quickly and often, and therefore provides a good simulation of a vehicle driving in an urban environment.

The experimental results obtained from the FRDT for Base Fuel A containing 60 PTB of commercial fuel additive and a motor fuel composition of the instant invention (Example IV) are set forth in Figure 1. As illustrated by Figure 1, the octane requirement of the engine using Base Fuel A containing 60 PTB of commercial fuel additive was consistently higher than the corresponding octane requirement of the engine using a motor fuel composition of the instant invention over the duration of the test. The one exception to this was the engine octane requirement results obtained for Run #2, where the octane requirement of Base Fuel A containing 60 PTB of commercial additive significantly decreased between 150 and 200 hours of engine operation (see Figure 1). However, this unusual result was due to engine ignition problems in Run #2, and does not detract from the superiority of the instant invention over a motor fuel containing a commercial fuel additive. The data set forth in Figure 1 thus indicate that a motor fuel composition of the instant invention has reduced ORI tendencies in comparison with a typical commercially available motor fuel composition.

The carburetor intake valve and intake manifold detergency properties of a commercially available motor fuel and a motor fuel composition of the instant invention (Example IV) were also measured via the Merit Rating Test. This test may be described as follows. At the end of a FRDT run for a given motor fuel composition, portions of the engine are dissassembled and various engine components are visually examined to determined the extent of deposit formation. This is determined via a visual rating system scaled from 1-10, with a value of 10 being a clean component and a value of 1 being a deposit-laden

component.

The experimental results obtained from the Merit Rating Test are set forth in Table I. As illustrated by Table I, a motor fuel composition of the instant invention is approximately as effective (based upon merit ratings) as a commercially available fuel. In addition, a motor fuel composition of the instant invention shows improved valve deposit control, in view of both valve merit rating and reduced valve deposit weight.

TABLE I

Chevy 1.8 liter Engine (FRDT) Merit Rating Results		
	Commercial Fuel	Instant Invention (Example IV)
Duration of Test Run (hours)	150	150
Merit Ratings:*		
Body	7.8	9.1
Primary	9.8	9.5
Secondary	5.8	8.7
Plate	8.4	8.2
Primary	9.8	8.4
Secondary	7.0	7.9
Man Runner	8.6	9.2
Head Runner	7.6	8.6
Head Ports	6.2	7.6
Valves	4.6	6.8
Valve Deposit Wt. (Mg)	1.8	0.5
Combustion Chamber	7.8	7.5
Piston	8.0	7.5

* Merit Rating of 10 = clean (no deposits)

The ORI tendencies of a commercially available gasoline and a motor fuel composition of the instant invention were also measured via the 2.0 liter Chevrolet (Throttle Body Injector) multicylinder engine test (Chevy Test). The Chevy Test employs a 2.0 liter Chevrolet in-line four cylinder engine with a cast alloy iron cylinder head having separate intake and exhaust ports for each cylinder. An electronically controlled fuel injection system maintains the required fuel flow to each engine cylinder by monitoring various engine operating parameters (e.g. manifold absolute pressure, throttle valve position, coolant temperature, engine r.p.m., the exhaust gas oxygen content) and adjusting the fuel flow accordingly. The fuel system supplying fuel to the engine is specifically adapted for the determination of engine ORI. At the beginning of the engine rating procedure, a fuel with an octane rating high enough to ensure that no audible engine knock is present is employed. The next lower octane fuel is then switched with the previous fuel, and this procedure continues until a knock becomes audible. The octane level one number above knock is the engine octane requirement. Engine ORI was determined as a function of hours of engine operation for both the commercial gasoline and a motor fuel composition of the instant invention.

As illustrated by Figure 2, the octane requirement of the engine using the commercial gasoline was consistently higher than the corresponding octane requirement of the engine using a motor fuel composition of the instant invention over the duration of the test. After about 200 hours of engine operation in the Chevy Test, the commercial gasoline gave an ORI number approximately 5-7 units higher than the instant invention. The data set forth in Figure 2 thus again indicate that a motor fuel composition of the instant invention has reduced ORI tendencies in comparison with a typical commercially available gasoline.

The carburetor, intake valve and intake manifold detergency properties of the commercial gasoline and a motor fuel composition of the instant invention (Example IV) were also compared via the Merit Rating Test. At the end of a Chevy Test run for a given motor fuel composition, portions of the engine are disassembled and various engine components are visually examined to determine the extent of the deposit formation. This is determined via a visual rating system scaled from 1-10, with a value of 10 being a clean component and a value of 1 being a deposit-laden component.

The experimental results obtained from the abovedescribed Merit Rating Test are set forth in Table II.

As illustrated by Table II, a motor fuel composition of the instant invention was approximately as effective (based upon merit ratings) as a commercially available gasoline. In addition, a motor fuel composition of the instant invention showed improved valve deposit control, both in terms of valve merit rating and reduced valve deposit weight.

TABLE II

Chevy 2.0 liter Engine (Chevy Test) Merit Rating Results		
	Commercial Gasoline	Instant Invention (Example IV)
Duration of Test Run (hours)	207	200
Merit Ratings:*		
Body	10.0	8.9
Plate	9.8	9.3
Manifold Runner	8.8	9.5
Head Runner	8.5	7.9
Head Parts	5.2	8.0
Valves	5.0	8.2
Valve Deposit Wt. (Mg)	1.9	0.3
Combustion Chamber	8.5	7.8
Piston Crown	8.4	8.0

* Merit Rating of 10 = clean (no deposits)

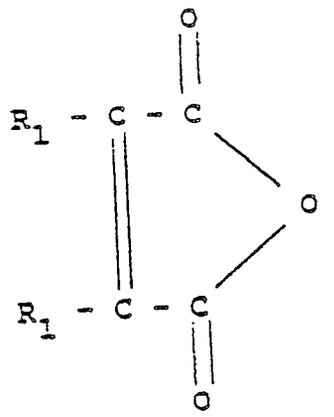
For convenience in shipping and handling, it is useful to prepare a concentrate of the reaction product and polyisobutylene ethylene diamine-polyisobutylene components of the instant invention. The concentration may be prepared in a suitable liquid solvent such as toluene and xylene, with xylene being preferred. In the best mode of preparing a concentrate of the instant invention, approximately 0.1-10.0, preferably 5.0-10.0 percent of the reaction product of Example I, and approximately 25.0-75.0, preferably 50.0-60.0 weight percent of the abovedescribed aromatic distillate-polyisobutylene ethylene diamine-polyisobutylene mixture are employed in admixture with 25.0-50.0, preferably 30.0-40.0 weight percent of aromatic hydrocarbons, preferably xylene. All weight percents are based upon the total weight of the concentrate.

It will be evident that the terms and expressions employed herein are used as terms of description and not of limitation. There is no intention, in the use of these descriptive terms and expressions, of excluding equivalents of the features described and it is recognized that various modifications are possible within the scope of the invention claimed.

Claims

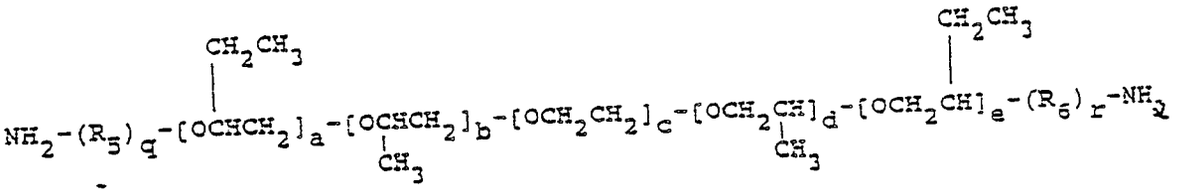
1. A composition characterised in that it comprises the reaction product obtained by reacting at a temperature of 30° C-200° C:

(a) about 1 mole of a dibasic acid anhydride of the formula



where R_1 is either H or a C_1-C_5 alkyl radical;

(b) 1-2 moles of a polyoxyalkylene diamine of the formula



where R_5 and R_6 are C_1-C_{12} alkylene groups, q and r are integers having a value of 0 or 1, c has a value from about 5-150, b + d has a value from about 5-150, and a + e has a value from about 2-12; and

(c) 1-2 moles of a hydrocarbyl polyamine which may be either:

(i) a hydrocarbyl polyamine of the formula

$R_2(NH\text{-}R_3)_x\text{ - }NH_2$

where R_2 is n alkyl radical having from about 1-24 carbon atoms, R_3 is an alkylene radical having from about 1-6 carbon atoms, and x has a value from about 1-10; or

(ii) a n-alkyl-alkylene diamine of the formula

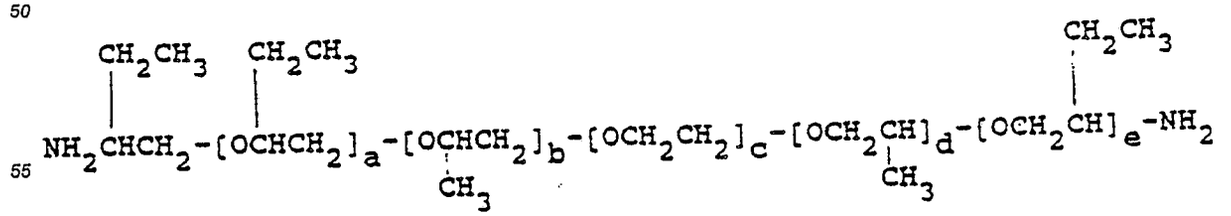
$R_4\text{-}NH\text{-}(CH_2)_n\text{-}NH_2$

where R_4 is an aliphatic hydrocarbon radical having from about 1-24 carbon atoms and n has a value from about 1-6.

2. A composition according to Claim 1 characterised in that said reaction product is obtained by reacting about 1 mole of said dibasic acid anhydride with about 1.5 moles of said polyoxyalkylene diamine and about 1 mole of said hydrocarbyl polyamine or n-alkyl-alkylene diamine.

3. A composition according to Claim 1 or Claim 2 characterised in that said dibasic acid anhydride reactant is maleic anhydride.

4. A composition according to any of the preceding Claims characterised in that said polyoxyalkylene diamine reactant is of the formula



where c has a value from about 8-50, b + d has a value from about 8-50, and a + e has a value from about 4-

8.

5. A composition according to any of the preceding claims, characterised in that said hydrocarbyl polyamine reactant is either:

(1) a hydrocarbyl polyamine of the formula:

$R_2(NE\text{-}R_3)_x\text{-}NE_2$

where R_2 is an alkyl radical having from about 12-20 carbon atoms, R_3 is an alkylene radical having from about 1-5 carbon atoms, and x has a value from 1-5 or

(11) a n-alkyl-alkylene diamine of the formula

$R_4\text{-}NH\text{-}(CH_2)_n\text{-}NH_2$

where R_4 is an aliphatic hydrocarbon radical having from about 12-20 carbon atoms, and n has a value of 3.

6. A composition according to Claim 5, characterised in that said n-alkyl-alkylene diamine reactant is selected from:
n-coco-1,3-diaminopropane;
n-soya-1,3-diaminopropane;
n-tallow-1,3-diaminopropane; and
n-oleyl-1,3-diaminopropane.

7. A concentrate composition characterised in that it comprises 1.0-75.0 weight percent of the reaction product of any of Claims 1 to 6 in admixture with a hydrocarbon solvent.

8. A concentrate composition characterised in that it comprises 5.0-35.0 weight percent of the reaction product of any of Claims 1-6 in admixture with a hydrocarbon solvent.

9. A major fuel composition according to any of Claims 1 to 6 characterised in that said composition comprises a mixture of hydrocarbons boiling in the range from about 30°C (90°F) to 230°C (450°F) and 0.0005-5.0 weight percent of a composition as claimed in any of Claims 1 to 6.

10. A composition according to Claim 9 characterised in that the reaction product additive is present in an amount of about 0.0001-1.0 weight percent.

11. A composition according to Claim 9, characterised in that the reaction product additive is present in an amount of about 0.01-0.1 weight percent.

12. A composition according to any of Claims 9 to 11, characterised in that the composition additionally comprises from about 0.001-1.0 weight percent of a polyolefin polymer, copolymer, or the corresponding hydrogenated polymer or copolymer, or mixtures thereof, of a C_2-C_6 unsaturated hydrocarbon, said polyolefin polymer or copolymer having a molecular weight in the range from about 500-3500.

13. A composition according to Claim 12, characterised in that said polyolefin polymer or copolymer component is derived from an unsaturated hydrocarbon selected from ethylene, propylene, isopropylene, butylene, isobutylene, amylene, hexylene, isoprene and butadiene.

14. A composition according to Claim 13, characterised in that said polyolefin polymer, copolymer, or corresponding hydrogenated polymer or copolymer component has a molecular weight in the range of about 650-2600.

15. A composition according to Claim 14, characterised in that said polyolefin polymer component is a polypropylene having a molecular weight in the range of about 750-1000.

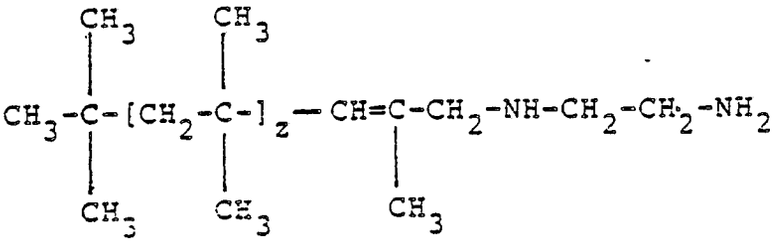
16. A composition according to Claim 15, characterised in that said polyolefin polymer component is a polypropylene with an average molecular weight of about 800.

17. A composition according to Claim 14, characterised in that said polyolefin polymer component is a polyisobutylene having a molecular weight in the range of about 1000-1500.

18. A composition according to Claim 17, characterised in that said polyolefin polymer component is a polyisobutylene having an average molecular weight of about 1300.

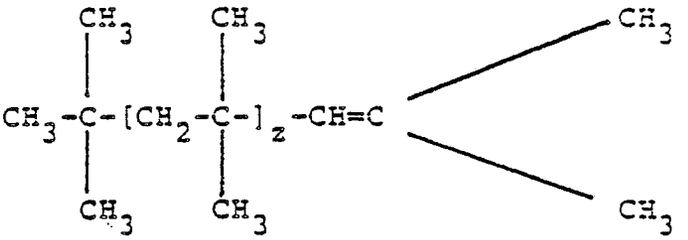
19. A composition according to any of Claims 12 to 18, characterised in that said polyolefin polymer or copolymer component is present in an amount of from about 0.01-0.5 weight percent.

20. A composition according to any of Claims 9 to 19, characterised in that the composition further comprises from 0.001-1.0 weight percent of a mixture comprising a hydrocarbon solvent and:
(a) 50-75 parts by weight of polyisobutylene ethylene diamine of the formula



and

(b) 5-25 parts by weight of polyisobutylene of the formula



where z has a value of 30-40.

21. A composition according to Claim 20, characterised in that z has a value of 32-35.

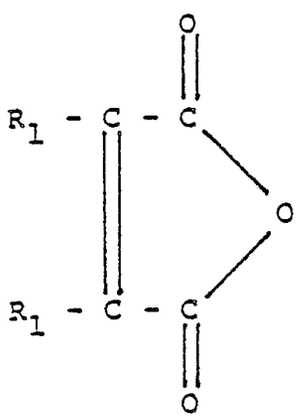
22. A composition according to Claim 20 or 21, characterised in that said hydrocarbon solvent is an aromatic distillate comprising xylene and C_9 alkylbenzene compounds.

23. A component according to any of Claims 20 to 22, characterised in that the composition includes from about 0.01-0.5 weight percent of a mixture comprising an aromatic distillate, about 60 parts by weight of said polyisobutylene ethylene diamine and about 10-20 parts by weight of said polyisobutylene, and in which z has a value of 32-35.

24. A concentrate composition, characterised in that it comprises a hydrocarbon solvent in admixture with:

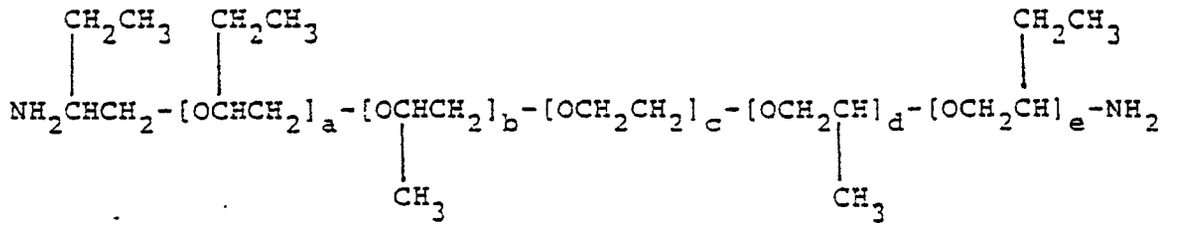
(I) from 0.1-10.0 weight percent of the reaction product obtained by reacting a temperature of 30° C-200° C:

(a) about 1 mole of a dibasic acid anhydride of the formula



where R_1 is H or a C_1-C_5 alkyl radical,

(b) 1-2 moles of a polyoxyalkylene diamine of the formula



where c has a value from about 5-150, b + d has a value from about 5-150, and a + e has a value from about 2-12, and

(c) 1-2 moles of a hydrocarbyl polyamine which may be either

(i) a hydrocarbyl polyamine of the formula

$R_2(NH\text{-}R_3)_x\text{-}\ NH_2$

where R_2 is an alkyl radical having from about 1-24 carbon atoms, R_3 is an alkylene radical having from about 1-6 carbon atoms, and x has a value from about 1-10, or

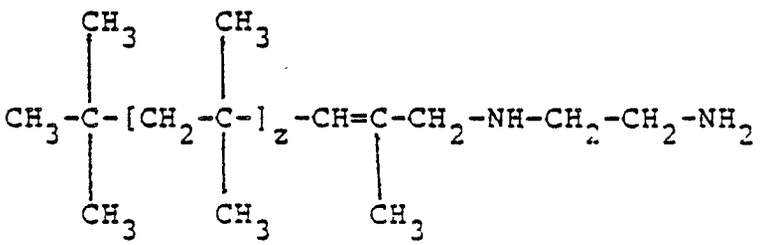
(ii) a n-alkyl-alkylene diamine of the formula

$R_4\text{-}NH\text{-}(CH_2)_n\text{-}NH_2$

where R_4 is an aliphatic hydrocarbon radical having from about 1-24 carbon atoms and n has a value from about 1-6; and

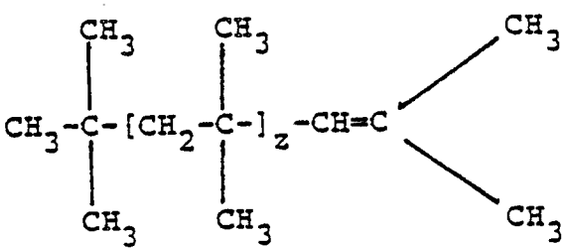
(II) from 25.0-75.0 weight percent of a mixture comprising a hydrocarbon solvent and:

(a) 50-75 parts by weight of polyisobutylene ethylene diamine of the formula



and

(b) 5-25 parts by weight of polyisobutylene of the formula



where z has a value of 30-40.

FIG. 1

OCTANE REQUIREMENT VS. HOURS OF ENGINE OPERATION
1983 CHEVROLET 2.0 LITER ENGINE (CHEVY TEST)

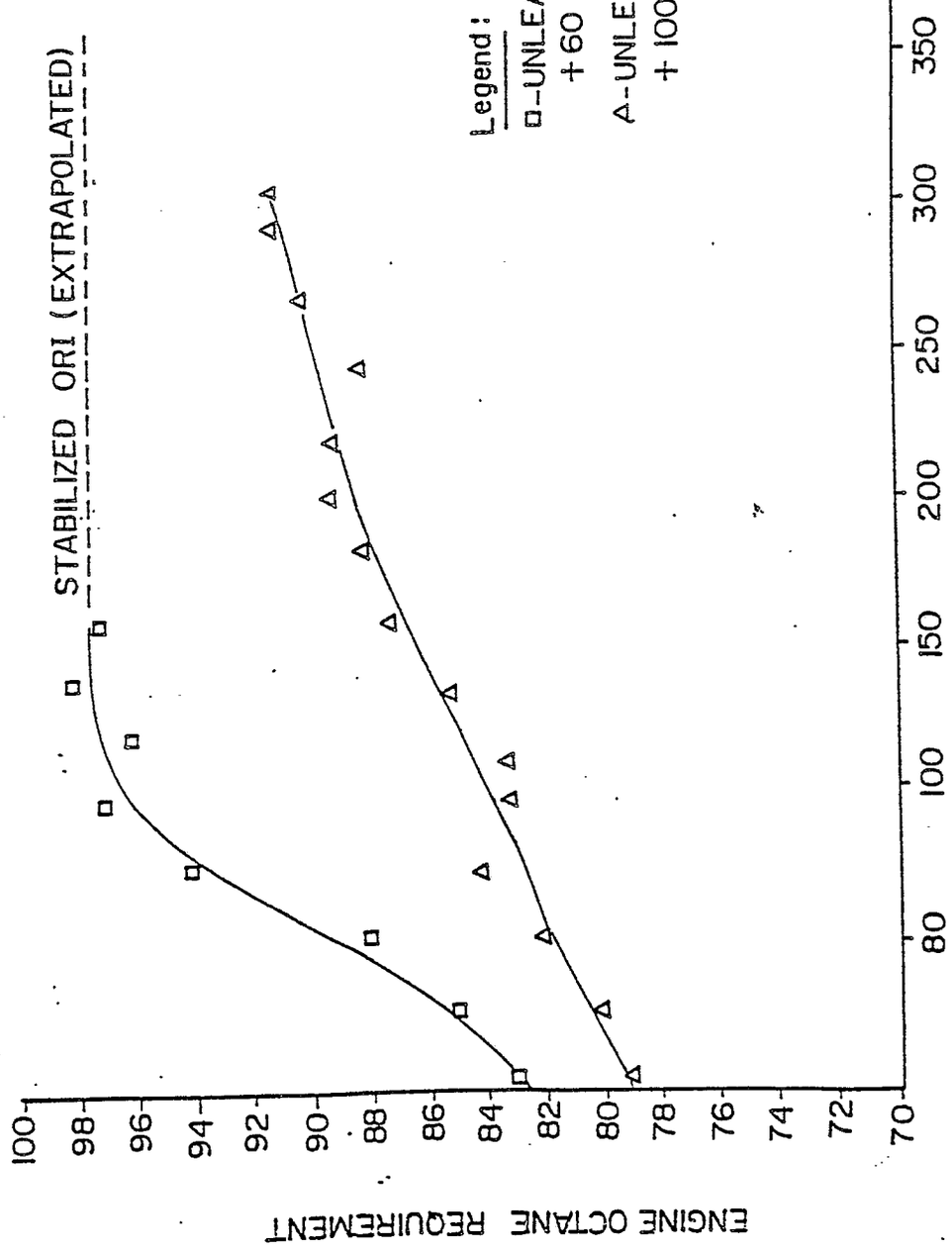


FIG. 2

OCTANE REQUIREMENT VS. HOURS OF ENGINE OPERATION
1983 CHEVROLET 2.0 LITER ENGINE (CHEVY TEST)

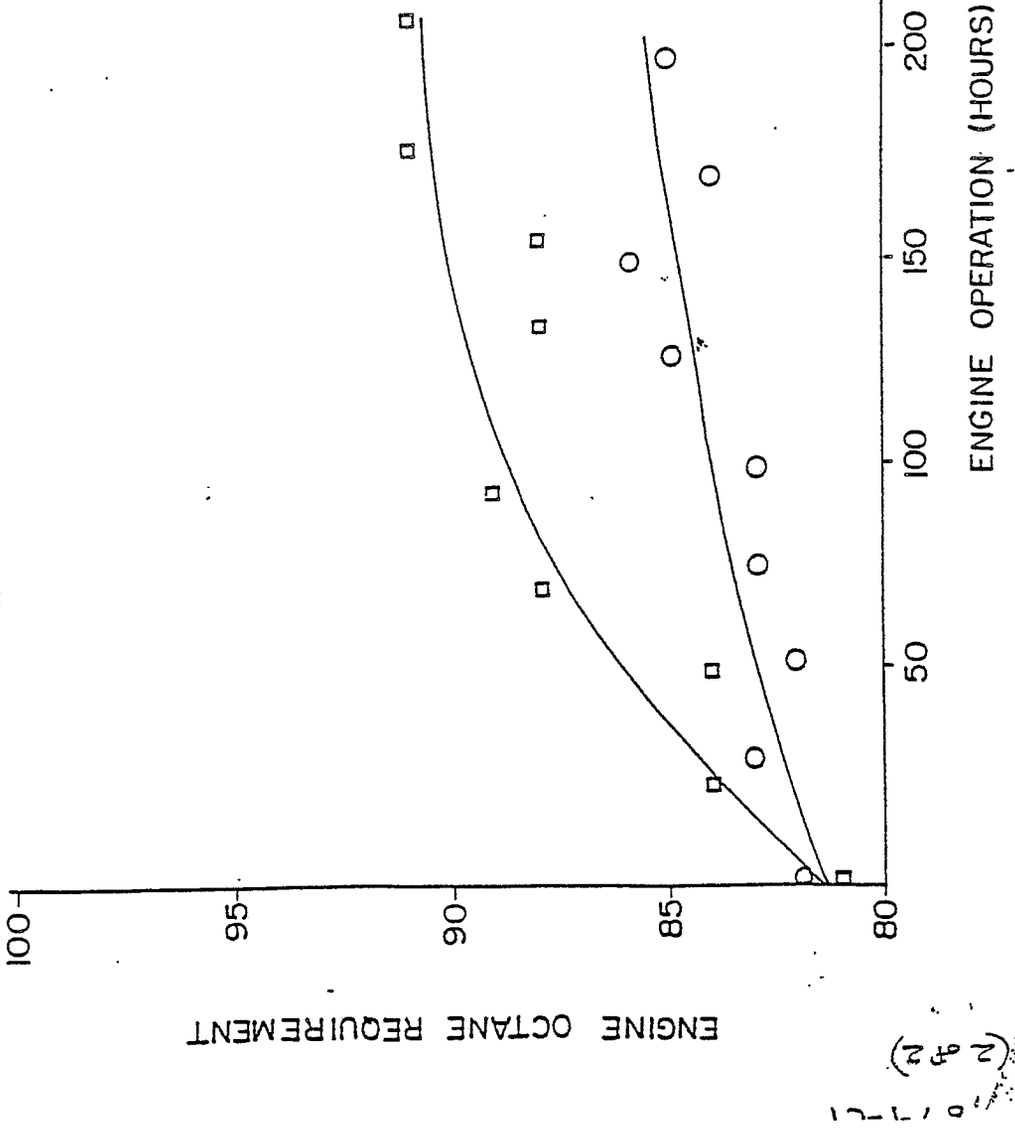
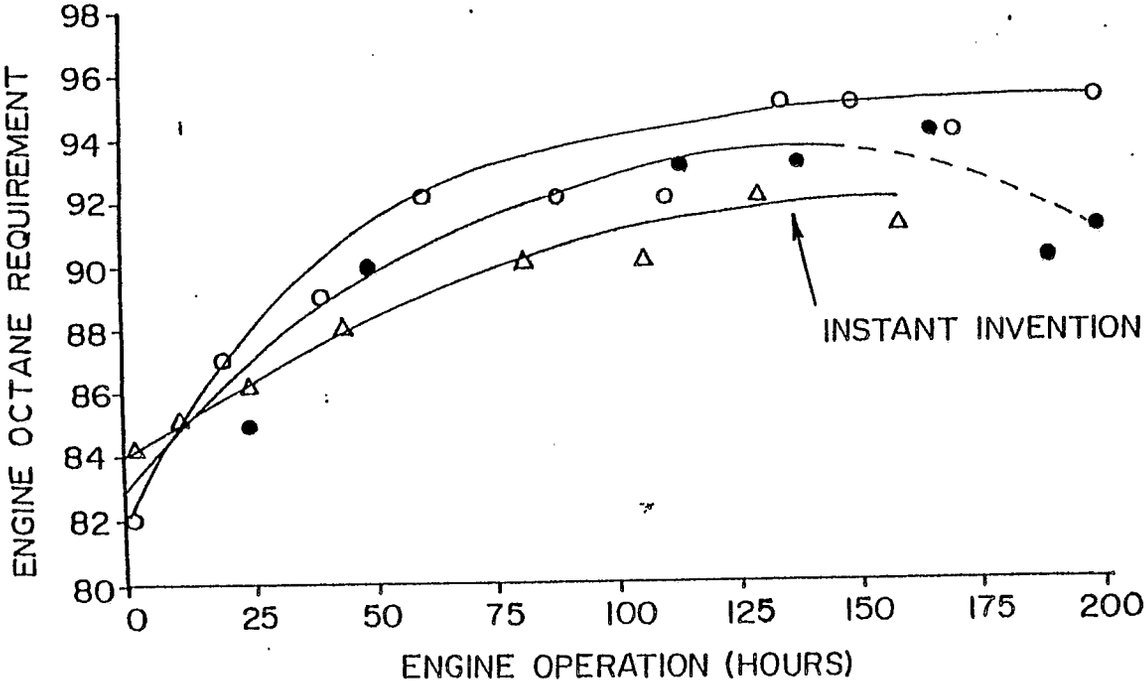


FIG. 3

ENGINE OCTANE REQUIREMENT VS. ENGINE OPERATION (HOURS) – FRDT



Legend:

Δ – INSTANT INVENTION (Example IV)

o – RUN #1 – BASE FUEL A+60 PTB COMMERCIAL ADDITIVE

● – RUN #2 – BASE FUEL A+60 PTB COMMERCIAL ADDITIV

IGNITION PROBLEMS IN RUN #2 DESIGNATED BY – – – – – –

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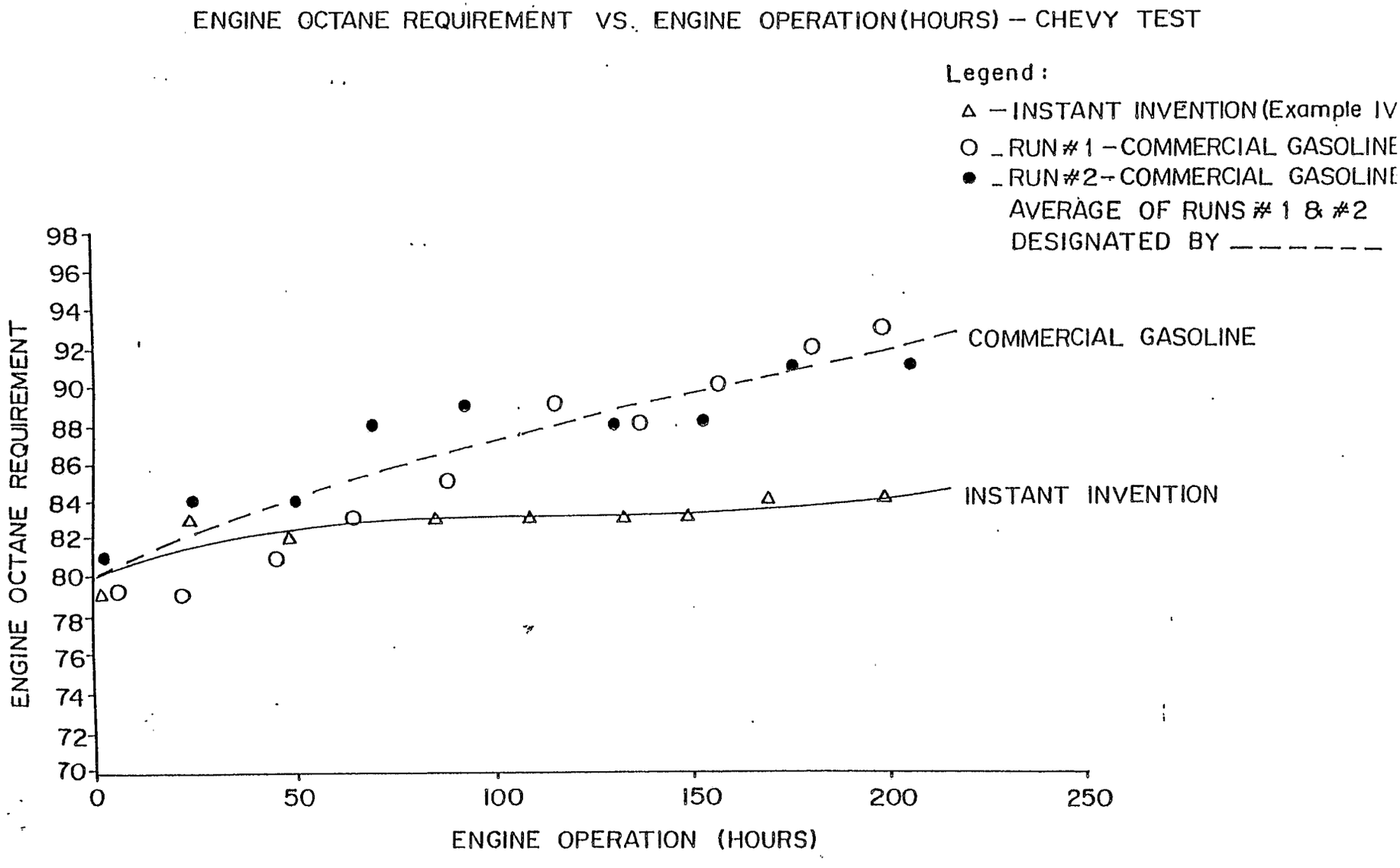
FIG. 4



EP 0 303 351 A1

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 88 30 6166

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
E	EP-A-0 273 545 (TEXACO) * Whole document *	1-19	C 10 L 1/22 C 10 L 1/14 C 08 G 65/32
A	US-A-4 141 693 (FELDMAN et al.) * Column 1,2 *	20-24	
D,A	US-A-4 659 336 (SUNG et al.) * Whole document *	1-24	
D,A	EP-A-0 208 978 (TEXACO) * Whole document * & US-A-4 659 337	1-24	
A	US-A-4 313 764 (TRACY et al.) * Whole document *	1	
A	EP-A-0 207 560 (SHELL) * Claims; column 4, lines 8-43; column 5, lines 14-43 *	20-24	
A	EP-A-0 062 940 (SHELL) * Abstract; claims; examples *	20-24	TECHNICAL FIELDS SEARCHED (Int. Cl.4)
D,A	US-A-3 960 515 (HONNEN) * Claims *	20-24	C 10 L C 08 G
D,A	GB-A-2 010 324 (CHEVRON) * Whole document * & US-A-4 166 726	20-24	
A	US-A-3 806 456 (VOGEL) * Whole document *	1-24	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	19-10-1988	DE LA MORINERIE B.M.S.B.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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E : earlier patent document, but published on, or after the filing date
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