

[54] FUEL COMPOSITIONS COMPRISING A COMBINATION OF OXY COMPOUNDS AND ASHLESS DISPERSANTS

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Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 749,948, Aug. 5, 1968, abandoned.

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[58] Field of Search 44/60, 70, 71, 77, 57, 63; 252/51.5 A

References Cited

UNITED STATES PATENTS

Table with 3 columns: Patent Number, Date, Inventor/Assignee. Includes entries for Callis (1/1938), Moore et al. (10/1950), Caron et al. (4/1951), and Stayner et al. (3/1957).

Table with 3 columns: Patent Number, Date, Inventor/Assignee. Includes entries for Foreman (9/1957), McGuire (7/1962), Norman et al. (7/1965), Norman et al. (11/1965), Brannen, Jr. (9/1967), and Le Seur (4/1968).

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[57] ABSTRACT

Fuel compositions containing an additive combination comprising an oxy compound and a dispersant. Oxy compounds include glycol, polyglycols, and carboxylic acid esters thereof and carboxylic acid esters of monoethers of glycols and polyglycols. The dispersants are the esters, amides, imides, amidines, amine salts, and mixtures thereof of carboxylic acids characterized by the presence of at least about 30, but preferably at least 50, aliphatic carbon atoms in the acyl moiety. Solutions of such additive combinations are also disclosed. The fuels and solutions can be used to clean fuel systems in liquid-fuel burning devices such as internal combustion engines.

18 Claims, No Drawings

### FUEL COMPOSITIONS COMPRISING A COMBINATION OF OXY COMPOUNDS AND ASHLESS DISPERSANTS

This is a continuation-in-part of copending application Ser. No. 749,948 filed Aug. 5, 1968, now abandoned.

This invention relates to compositions of matter and methods for using such compositions. Particularly, the invention is concerned with fuel compositions and methods for cleaning the fuel systems of liquid fuel-burning engines and other fuel-burning devices such as furnaces. This invention is based upon the discovery that certain oxy compounds in combination with certain dispersants are very useful in inhibiting and removing sludge and other deposits which accumulate in such fuel systems. As is well known, the means for eliminating and inhibiting the formation of undesirable deposits within the fuel systems of engines and the like are constantly being sought.

In accordance with the foregoing, it is a principal object of this invention to provide novel fuel compositions.

Another object is to provide fuel compositions containing an additive combination consisting of oxy compounds and certain dispersants.

A still further object of this invention is to provide methods for cleaning the fuel systems of internal combustion engines and other liquid-fuel burning devices through the use of the additive combination of this invention.

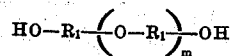
These as well as other objects of this invention are achieved by providing fuel compositions comprising a major amount of at least one normally liquid fuel, generally a petroleum distillate fuel, and a minor amount of an additive combination soluble in said fuel, the additive combination comprising at least one oxy compound selected from the class consisting of glycols, polyglycols, and the carboxylic acid esters of these glycols, polyglycols, and their monoethers with monocarboxylic acid containing up to about twenty carbon atoms, and at least one fuel-soluble dispersant selected from the class consisting of esters, amides, imides, amidines, and amine salts of at least one substantially saturated carboxylic acid characterized by the presence within the acyl radical thereof of at least 30 aliphatic carbon atoms; the weight ratio of oxy compound to dispersant being about 1:10 to about 10:1. The method for cleaning fuel systems as contemplated by this invention is readily achieved by contacting fuel compositions of this type with at least the internal surfaces of said fuel systems. The cleaning method can also be accomplished by using the additive combination in the form of a non-fuel solution thereof as a cleaning material.

The additive combination used in the fuel compositions of this invention consists of two essential components: at least one oxy compound and at least one ashless dispersant. The additive combination may be dissolved in a mutual solvent prior to adding it to the fuel although this is not essential and the additive components can be added directly to the fuel composition. Obviously, the additive combination should be soluble in the particular fuel in which it is to be used. However, the solubility of the combination usually presents no problem since the dispersants are readily soluble in the fuels and the oxy compounds are at least partially soluble in the fuel. However, one of the attributes of the additive combination is that the dispersants promote the increased solubility of the oxy compounds so that a combination of the dispersant and oxy compound is soluble in fuel even though the oxy compound alone may not be sufficiently soluble. Furthermore, the weight ratio of the oxy compound and dispersant is flexible so that the amount of each can be varied greatly in order to achieve solubility of an additive combination for a given fuel composition.

The oxy compounds contemplated as components in the additive combination in this invention are well known in the art and can be readily synthesized according to known procedures or obtained commercially from various chemical suppliers. The term "glycol" as used in the present specification and claims is intended to describe dihydric organic compounds of the formula  $\text{HO}-\text{R}_1-\text{OH}$  wherein  $\text{R}_1$  is a divalent hydrocarbon or substituted hydrocarbon radical. Thus,  $\text{R}_1$  can be alkylene, phenylene, cyclohexylene, or a substituted varia-

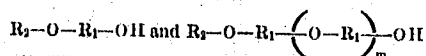
tion of one of these wherein the substituent is lower alkyl, lower alkoxy, nitro, halo, oxo, and the like. Representative substituted radicals would include 2-(ethoxy)-hexamethylene; 3-chloro-phenylene-1,3; 2-(methoxy)-phenylene-1,4; and 4-(n-butoxy)-cyclohexylene-1,2. However, from the standpoint of availability and economy, it is preferred that the  $\text{R}_1$  variable be a divalent hydrocarbon radical, particularly an aliphatic hydrocarbon radical.

The terminology "polyglycols" as used in the present specification and claims is intended to describe the polyethers prepared from such glycols. Thus, the polyglycols could be represented by the formula



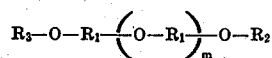
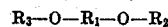
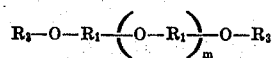
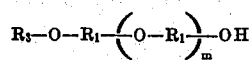
where each  $\text{R}_1$  is independently a divalent radical of the type described above and  $m$  is at least one.

The oxy compounds contemplated by the present invention also included the carboxylic acid esters of the glycols and polyglycols described hereinabove and their monoethers. These monoethers can be represented by the formula



wherein  $\text{R}_2$  is a monovalent hydrocarbon or substituted hydrocarbon radical and  $\text{R}_1$  and  $m$  are as defined above. Thus,  $\text{R}_2$  can be an aliphatic, cycloaliphatic, or aromatic hydrocarbon group or a substituted hydrocarbon group of this type wherein the substituents are the same as those mentioned above in the case of  $\text{R}_1$ . Again,  $\text{R}_2$  will usually be a hydrocarbon radical, particularly an alkyl radical or a phenyl radical including alkyl phenyl radicals. Illustrative examples of  $\text{R}_2$  include methyl, ethyl, propyl, isopropyl, butyl, tertiary butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, phenyl, benzyl, tolyl, xylyl, phenethyl, p-methoxy-phenyl, cyclohexyl, cyclopentyl, and the like.

The esters of the foregoing glycols, polyglycols, and their monoethers are illustrated by compounds corresponding to the formulas

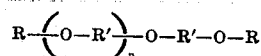


where  $\text{R}_3$  is a monovalent carboxylic acid acyl radical containing up to about 20 carbon atoms and where  $\text{R}_1$ ,  $\text{R}_2$ , and  $m$  are as defined hereinbefore. The acyl radical may be the radical of a monocarboxylic aliphatic, cycloaliphatic, or aromatic acid. Thus, the radical  $\text{R}_3$  corresponds to the formula



where  $\text{R}_4$  is a hydrocarbon or substituted hydrocarbon radical of up to 19 carbon atoms. Illustrative examples of the radical  $\text{R}_3$  include formyl, acetyl, propionyl, and the corresponding acyl radicals derived from such acids as acetic, propionic, butyric, valeric, caproic, enanthic, caprylic, pelargonic, capric, lauric, myristic, palmitic, stearic, isostearic benzoic, and phenylacetic acid or cyclopentyl or cyclohexyl carboxylic acids and the like. Preferably the acyl radical is derived from an aliphatic monocarboxylic acid, particularly alkanolic acids. The lower alkanolic monocarboxylic acids are especially preferred group of acids.

A particularly preferred class of oxy compounds is represented by the formula



where  $n$  is such that the average molecular weight of the oxy compounds is not greater than about 1,200, each  $R$  is independently selected from the class consisting of hydrogen or a monocarboxylic acid acyl radical of up to about twenty carbon atoms and  $R'$  is hydrocarbylene of up to about eight carbon atoms. The hydrocarbylene groups may be aliphatic, cycloaliphatic or aromatic groups. Preferably, however, the hydrocarbylene groups will be branched or straight chain saturated aliphatic groups. An especially preferred class of oxy compounds are those corresponding to the above formula wherein  $n$  is 0, 1, 2, or 3, each  $R$  is independently H or acyl with the proviso that at least one  $R$  variable is acyl and  $R'$  is alkylene of up to about eight carbon atoms.

Specific examples of oxy compounds falling within the ambit of the above formulae are ethylene glycol, propylene glycol, trimethylene glycol, alpha-butylene glycol, 1,3-butanediol, beta-butylene glycol, isobutylene glycol, tetramethylene glycol, hexylene glycol, diethylene glycol, dipropylene glycol, tripropylene glycol, triethylene glycol, tetraethylene glycol, 1,5-pentanediol, 2-methyl-2-ethyl-1,3-propane diol, 2-ethyl-1,3-hexanediol, the carboxylic acid esters thereof as described above and the corresponding esters of their monoesters, e.g., ethylene glycol mono phenyl ether, ethylene glycol mono methyl ether, ethylene glycol mono ethyl ether, ethylene glycol mono *n*-butyl ether, diethylene glycol mono methyl ether, diethylene glycol mono ethyl ether, diethylene glycol mono *n*-butyl ether, propylene glycol mono methyl ether, dipropylene glycol mono methyl ether, tripropylene glycol mono methyl ether, ethylene glycol mono isopropyl ether, ethylene glycol mono isobutyl ether, ethylene glycol mono hexyl ether, triethylene glycol mono butyl ether, triethylene glycol mono methyl ether, triethylene glycol mono ethyl ether, 1-butoxyethoxy-2-propanol, polypropylene glycol having an average molecular weight of about 975-1075, monophenyl ether of polypropylene glycol wherein the polyglycol has an average molecular weight of about 400-450 monophenyl ether of polypropylene glycol wherein the polypropylene glycol has an average molecular weight of 975-1075. Specific esters include acrylic acid ester of 2-ethoxy-ethanol, valeric acid diester of diethylene glycol, ethylene glycol diacetate, ethylene glycol monoacetate, the dicaproic acid ester of diethylene glycol, and the like. Such oxy compounds are sold in commerce under such names as Butyl CELLOSOLVE, Ethyl CELLOSOLVE, Hexyl CELLOSOLVE, DOWANOL Glycol Ethers, and the like. Such compounds are also disclosed in U.S. Pat. Nos. 2,089,580; 2,786,745; 2,807,525; 2,807,526; 2,914,479; 3,030,939; 3,061,420; etc.

The second essential component of the additive combination is the dispersant. These dispersants are the esters, amides, imides, amidines and amine salts of certain high molecular weight mono and polycarboxylic acids, these carboxylic acids being characterized by the presence within the acyl moieties thereof of at least about thirty aliphatic carbon atoms. These dispersants are well known to those skilled in the art and have achieved widespread use in recent years as ashless additives for lubricating oils. Dispersants of this type and methods for their preparation are disclosed in detail in the following U.S. Pat. Nos. 3,172,892; 3,184,474; 3,194,814; 3,194,812; 3,219,666; 3,272,746; 3,340,281; 3,341,542; 3,347,645; 3,361,673; 3,381,022; British patent 981,850; British patent 1055,337. For the sake of brevity, these patents are expressly incorporated herein for their disclosure of ashless dispersants and processes for preparing them. Generally, these dispersants are prepared by reacting a mono or polycarboxylic acid acylating agent with a suitable hydroxy- or amino-compound.

As disclosed in the above incorporated patents, there are several processes for preparing the acylating agents. Generally, the process involves the reaction of (1) an ethylenically unsaturated carboxylic acid, acid halide, acid ester, or anhydride with (2) an ethylenically unsaturated hydrocarbon containing at least about 50 aliphatic carbon atoms or a chlorinated hydrocarbon containing at least about 30 aliphatic

carbon atoms at a temperature within the range of about 100°-300° C. The chlorinated hydrocarbon or ethylenically unsaturated hydrocarbon reactant can, of course, contain polar substituents, oil-solubilizing pendant groups, and be unsaturated within the general limitations explained hereinabove. It is these hydrocarbon reactants which provides most of the aliphatic carbon atoms present in the acyl moiety of the final products.

When preparing the carboxylic acid acylating agent according to one of these two processes, the carboxylic acid reactant usually corresponds to the formula  $R_0-(COOH)_n$ , where  $R_0$  is characterized by the presence of at least one ethylenically unsaturated carbon-to-carbon covalent bond and  $n$  is an integer from 1 to 6 and preferably 1 or 2. The acidic reactant can also be the corresponding carboxylic acid halide, anhydride, ester (usually the lower alkyl esters) or other equivalent acylating agent and mixtures of one or more of these. Ordinarily, the total number of carbon atoms in the acidic reactant will not exceed 10 and generally will not exceed 6. Preferably the acidic reactant will have at least one ethylenic linkage in an  $\alpha\beta$ -position with respect to at least one carboxyl function. Exemplary acidic reactants are acrylic acid, methacrylic acid, maleic acid, maleic anhydride, fumaric acid, itaconic acid, itaconic anhydride, citraconic acid, citraconic anhydride, mesaconic acid, glutaconic acid, chloromaleic acid, aconitic acid, crotonic acid, methylcrotonic acid, sorbic acid, 3-hexenoic acid, 10-decenoic acid, and the like. Due to such considerations as economy, availability, reactivity, and performance of the products, the acid reactants usually employed are  $\alpha\beta$ -unsaturated mono and dicarboxylic acids, particularly fumaric acid, and maleic anhydride, acrylic acid, and methacrylic acid.

The carboxylic acid acylating agents may contain cyclic and/or aromatic groups. However, the acids are preferably essentially aliphatic in nature. The most preferred acylating agents are the aliphatic carboxylic acids, anhydrides, esters or halides, usually the chlorides.

The substantially saturated aliphatic hydrocarbon-substituted succinic acids and anhydrides are especially preferred as acylating agents. These succinic acid acylating agents are readily prepared by reacting maleic anhydride with a high molecular weight olefin or a chlorinated hydrocarbon such as a chlorinated polyolefin. The reaction involves merely heating the two reactants at a temperature of about 100°-300° C., preferably, 100°-200° C. The product from such a reaction is a substituted succinic anhydride where the substituent is derived from the olefin or chlorinated hydrocarbon as described in the above cited patents. The product may be hydrogenated to remove all or a portion of any ethylenically unsaturated covalent linkages remaining by standard hydrogenation procedures, if desired. The substituted succinic anhydrides may be hydrolyzed by treatment with water or steam to the corresponding acid and either the anhydride or the acid may be converted to the corresponding acid halide or ester by reacting with phosphorus halide or lower alkanols.

The ethylenically unsaturated hydrocarbon reactant and the chlorinated hydrocarbon reactant used in the preparation of the acylating agents are principally the high molecular weight, substantially saturated petroleum fractions and substantially saturated olefin polymers and the corresponding chlorinated products. The polymers and chlorinated polymers derived from mono-olefins having from two to about 30 carbon atoms are preferred. The especially useful polymers are the polymers of 1-mono-olefins such as ethylene, propylene, 1-butene, isobutene, 1-hexene, 1-octene, 2-methyl-1-heptene, 3-cyclohexyl-1-butene, and 2-methyl-5-propyl-1-hexene. Polymers of medial olefins, i.e., olefins in which the olefinic linkage is not at the terminal position, likewise are useful. These are exemplified by 2-butene, 3-pentene, and 4-octene.

The interpolymers of 1-mono-olefins such as illustrated above with each other and with other interpolymerizable olefinic substances such as aromatic olefins, cyclic olefins, and polyolefins, are also useful sources of the ethylenically unsatu-

rated reactant. Such interpolymers include for example, those prepared by polymerizing isobutene with styrene, isobutene with butadiene, propene with isoprene, propene with isobutene, ethylene with piperylene, isobutene with chloroprene, isobutene with p-methyl-styrene, 1-hexene with 1,3-hexadiene, 1-octene with 1-hexene, 1-heptene with 1-pentene, 3-methyl-1-butene with 1-octene, 3,3-dimethyl-1-pentene with 1-hexene, isobutene with styrene and piperylene, isobutene with propylene, etc.

For reasons of oil-solubility and stability, the polymers contemplated for use in preparing the acylating agents of this invention should be substantially aliphatic and substantially saturated, that is, they should contain at least about 80 percent and preferably about 95 percent, on a weight basis, of units derived from aliphatic mono-olefins. They usually will contain no more than about 5 percent, preferably no more than about 2 percent, olefinic linkages based on the total number of the carbon-to-carbon covalent linkages present therein.

The chlorinated hydrocarbons and ethylenically unsaturated hydrocarbons used in the preparation of the acylating agents can have molecular weights of from about 300 up to about 10,000. The above described polyolefins and chlorinated polyolefins having an average molecular weight of about 400 to about 5,000 are preferred for preparing the acylating agents while those having molecular weights of about 700 to about 3000 are especially preferred. Polypropylene, polyisobutylene, copolymers of propylene and isobutylene and their chlorinated derivatives are particularly useful for reacting with the unsaturated acid compound to prepare suitable acylating agents. Other methods for preparing suitable carboxylic acid acylating agents useful as intermediates in the synthesis of the dispersants are disclosed in the above-incorporated patents.

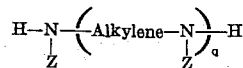
The dispersants are prepared by reacting at least one of the above-discussed acylating agents with a suitable hydroxyl compound or amino compound characterized by the presence within its structure of at least one-NH group. When the acylating agents are reacted with hydroxyl compounds, esters are produced whereas reaction with amino compounds produces amides, imides, amidines, amine salts, or mixtures thereof. If the reactant contains both hydroxyl and amino groups, the reaction mixture is usually a mixture of esters and acylated nitrogen compounds, i.e., amides, imides, amine salts, etc. Similarly, the acylating agents can be reacted with a mixture of hydroxyl compounds and amino compounds as disclosed in U.S. Pat. No. 3,184,474.

A preferred group of ester dispersants are those prepared from the polyolefin-substituted succinic acids or chlorinated polyolefin-substituted succinic acids and polyhydric alcohols containing up to about forty aliphatic carbon atoms and two-ten hydroxyl groups. The esters can be the mono or diesters or mixtures thereof. Esters of polyisobutenyl-substituted succinic acid and ethylene glycol, glycerol, pentaerythritol, mannitol, sorbitol, and the like are illustrative of this class of esters. Esters of this type are described in detail in U.S. Pat. No. 3,381,022 and British patents 981,850 and 1,055,337.

However, for purposes of this invention, the dispersant is preferably one prepared by reacting at least one of the above described acylating agents with an amino compound. As disclosed in U.S. Pat. No. 3,219,666, the amino compounds can be quite diversified and include aliphatic, cycloaliphatic, aromatic, and heterocyclic amines. These are exemplified by N-methyloctyl amine, N-cyclohexyl aniline, cyclohexyl amine, aniline, dodecyl amine, morpholine, piperazine, ethanol amine, phenol hydrazine, octadecyl hydrazine, urea, N-butyl urea, dicyan diamide, and the like. Generally, however, the amine is an alkylene polyamine. The dispersants of the present invention also include the reaction products of acylated nitrogen compounds prepared by reacting the above acylating agents with these amino compounds and other materials such as boron reactants as disclosed in U.S. Pat. No. 3,087,936;

carbon disulfide as disclosed in U.S. Pat. No. 3,200,107, alkenyl cyanide such as disclosed in U.S. Pat. No. 3,278,550; epoxides as disclosed in U.S. Pat. No. 3,373,111; dicarboxylic acids as disclosed in U.S. Pat. No. 3,374,174; monocarboxylic acids such as illustrated in U.S. Pat. Nos. 3,185,704 and 3,216,936; and aldehydes and ketones as disclosed in British Patent Specification 1,106,227. This last specification also discloses the reaction of these acylated amine materials with other reactive agents such as carboxylic acids, urea, thiourea, guanidine and boric acid. Again, for the sake of brevity, these patents are incorporated herein by reference for their disclosure of these various dispersants prepared from acylating agents and amino compounds. For the most part, these dispersants can be described as oil-soluble acylated nitrogen compounds characterized by the presence within their structure of a substantially saturated hydrocarbon-substituted polar group selected from the class consisting of acyl, acylimido, and acyloxy radicals wherein the substantially saturated hydrocarbon substituent contains at least about thirty aliphatic carbon atoms and a nitrogen-containing group characterized by a nitrogen atom attached directly to said polar radical.

The preferred dispersants are those prepared from monocarboxylic acid acylating agents and polyolefin substituted or chlorinated substituted succinic acids or anhydrides and alkylene polyamines. The polyolefin substituent can be hydrogenated according to known procedures to produce alkyl substituents if desired. The preparation of such compounds is disclosed in detail in U.S. Pat. Nos. 3,172,892; 3,219,666; 3,361,673; and 3,272,746. These especially preferred dispersants are prepared by reacting a monocarboxylic acid acylating agent or the substituted succinic acid acylating agent with an alkylene polyamine of the formula



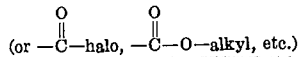
where  $q$  is an integer of 1-9 and  $Z$  is lower alkyl or H in a ratio of acylating agent to alkylene polyamine of one equivalent of acylating agent to one equivalent of alkylene polyamine to about one equivalent of acylating agent to one mole of alkylene polyamine. The reaction is generally conducted by heating a mixture of the acylating agent and the alkylene polyamine at a temperature of above about 80° C. and preferably within the range of 100° C. to about 250° C. The reaction may be conducted in the presence of a solvent such as benzene, toluene, naphtha, mineral oil, xylene, n-hexane, chlorobenzene, and the like. The reaction product is generally a mixture of amides, imides, amidines, and amine salts. Generally, however, if the reaction temperature is at least 100° C., the products consist essentially of the amides, imides, or amidines.

The alkylene polyamines from which the dispersants are prepared generally have less than eight carbon atoms in the alkylene moiety and usually two to four carbon atoms in the alkylene moiety. These alkylene amines include methylene amines, ethylene amines, propylene amines, butylene amines, pentylene amines, hexylene amines, and the like. Illustrative of this class of alkylene polyamines are ethylene diamine, triethylene tetramine, propylene diamine, decamethylene diamine, octamethylene diamine, di(heptamethylene)triamine, tripropylene tetramine, tetraethylene pentamine, pentaethylene hexamine, trimethylene diamine, diethylene triamine, and the like.

The ethylene polyamines are particularly preferred for preparing the dispersants. Included within the class of these ethylene polyamines are the commercially available mixtures of such ethylene polyamines prepared by the reaction of an alkylene chloride with ammonia. This reaction product consists of a mixture of ethylene polyamine such as tetraethylene pentamine, triethylene tetramine, diethylene triamine, pentaethylene hexamine, and the like as well as cyclic derivatives such as N-aminoethyl-piperazine, and the like.

Basic dispersants are particularly suitable in the additive combination of this invention. These basic dispersants are those prepared from a reaction mixture wherein the equivalent ratio of acylating agent to alkylene polyamine is at least 1:1.05. These basic dispersants are prepared generally by reacting the carboxylic acid acylating agents and the alkylene polyamines in a ratio of 1:1.1 to about 1:3.

For purposes of this invention, the number of equivalents in an amine reactant is that number of NH groups present therein. Similarly, an acylating agent has a number of equivalents per molecule corresponding to the number of carboxy groups



present. Thus, ethylene diamine has two equivalents; polyisobutenyl-substituted succinic acid, two; polyisobutenyl-substituted acrylic, one; tetraethylene pentamine, five; etc.

As mentioned hereinbefore, the fuel compositions of this invention can be prepared from solutions of the oxy compounds and the dispersants. Solvents useful in preparing such solutions are the normally liquid, substantially inert organic compounds such as the aliphatic, cycloaliphatic and aromatic hydrocarbons and chlorinated hydrocarbons, ethers, naphthas, mineral oils, N,N-dialkyl lower alkanolic acid amines, and the like. Illustrative solvents include kerosene, SAE 10 mineral oil, benzene, toluene, xylene, chlorobenzene, methoxybenzenes, ethoxybenzenes, pentane, hexane, heptane, octane, nonane, decane, undecane, dodecane, cyclohexane, cyclopentane, N,N-dimethylformamide, N,N-dimethylacetamide, ethyl ether, propyl ether, isopropyl ether, butyl ether, isoamyl ether, isobutyl ether, methyl n-propyl ether, methyl isobutyl ether, methylamyl ether, ethyl n-butyl ether, and the like. The best solvent or combination of solvents to be used with any additive combination will depend upon the particular dispersants, oxy compounds, and the fuel in which the additive is to be used. Generally speaking, the aromatic solvents particularly the aromatic hydrocarbons containing up to 12 carbon atoms such as benzene, toluene, xylene, and the like and combinations of these with each other or with the other types of solvents produce the best results.

The fuel compositions of this invention will comprise a major amount of a particular fuel and a minor amount of the additive combinations described hereinabove. Ordinarily, the additive combination will be present in an amount such that the total weight of dispersant and oxy compound present in the final fuel compositions will be from about 0.001 to about 5 percent by weight of the total weight of fuel and additive combination. A preferred concentration in fuels such as gasoline is 0.01 to about 1 percent by weight.

However, solutions of the additive combination of this invention can be used directly as cleaning agents for fuel systems. In other words, these additive combinations in the form of solutions in one or more of the above solvents can be used as a cleaning agent to clean the fuel systems of various internal combustion engines and other liquid fuel burning devices such as furnaces simply by contacting the internal surfaces of the fuel system with the solution. Since the combustion characteristics of these cleaning compositions is unimportant as they are not themselves to be burned, the additive combination can constitute a much larger portion of the cleaning composition, for example up to about 90 percent by weight of the total composition usually from about 5 percent up to about 70 percent by weight of the composition. It will be apparent to those skilled in the art, however, that even though such cleaning compositions are not intended to be burned, they can utilize fuels as solvents for the additive combination. Therefore, diesel fuel, kerosene, and gasoline solutions of the additive combination are contemplated as being cleaning compositions falling within the scope of the present invention.

In accordance with the foregoing, this invention contemplates the cleaning of the fuel system components of internal combustion engines such as the carburetor, fuel lines, fuel tank, filters, fuel pumps, fuel injectors, fuel metering devices, and the like either by employing a fuel containing the additive combination of this invention so that the internal surfaces of the various fuel system components can be cleaned by exposure to the additive combination in solution in the fuel or by contacting the internal surfaces of these components with a cleaning solution of the additive combination of this invention. It is also contemplated that the additive combination of this invention can be used as a fuel system cleaner in the same manner as other additive combinations presently on the market. That is, a solution of the additive combination may be added directly to the carburetor during, before, or after engine operation.

Members of the preferred class of dispersants, that is those prepared from alkylene polyamines, can be prepared according to the processes illustrated by the following examples. Other dispersants of the type contemplated by the present invention can be prepared according to the procedures set forth in detail in the above-incorporated patents. As used in the following examples and elsewhere herein, "percentages" and "parts" refer to per cent by weight and parts by weight unless otherwise indicated.

#### EXAMPLE 1

A polyisobutenyl succinic anhydride is prepared by the reaction of a chlorinated polyisobutylene with maleic anhydride at 200° C. The polyisobutenyl radical has an average molecular weight of 850 and the resulting alkenyl succinic anhydride is found to have an acid number of 113 (corresponding to an equivalent weight of 500). To a mixture of 500 grams (1 equivalent) of this polyisobutenyl succinic hydride and 160 grams of toluene there is added at room temperature 35 grams (1 equivalent) of diethylene triamine. The addition is made portionwise throughout a period of 15 minutes, and an initial exothermic reaction caused the temperature to rise to 50° C. The mixture then is heated and a water-toluene azeotrope distilled from the mixture. When no more water would distill the mixture is heated to 150° C. at reduced pressure to remove the toluene. The residue is diluted with 350 grams of mineral oil and this solution is found to have a nitrogen content of 1.6 percent.

#### EXAMPLE 2

The procedure of Example 1 is repeated using 55.5 grams (1.5 equivalents) of an ethylene amine mixture having a composition corresponding to that of triethylene tetramine. The resulting product has a nitrogen content of 1.9 percent.

#### EXAMPLE 3

To a mixture of 140 grams of toluene and 400 grams (0.78 equivalent) of a polyisobutenyl succinic anhydride (having an acid number of 109 and prepared from maleic anhydride and the chlorinated polyisobutylene of Example 1) there is added at room temperature 62.6 grams (1.55 equivalents) of an ethylene amine mixture having an average composition corresponding to that of tetraethylene pentamine. The mixture is heated to distill the water-toluene azeotrope and then to 150° C. at reduced pressure to remove the remaining toluene. The reaction product has a nitrogen content of 4.7 percent.

#### EXAMPLE 4

A mixture of 1056 grams (2.0 equivalents) of the polyisobutenyl succinic anhydride of the preceding example (in which the polyisobutenyl group has a molecular weight of 850), 89 grams (2.0 equivalents) of di-(1,2-propylene) triamine (having a nitrogen content of 31.3 percent), 370 grams of mineral oil and 100 grams of toluene is heated at reflux temperature (180°-90° C.) for 5 hours. A total of 18 grams of water is col-

lected from the water-toluene azeotrope. The residue is heated to 150° C./20 mm. to remove any last traces of water which might have remained. The nitrogen analysis of this residue is 1.9 percent.

#### EXAMPLE 5

A polypropylene-substituted succinic anhydride having an acid number of 84 is prepared by the reaction of a chlorinated polypropylene having a chlorine content of 3 percent and molecular weight of 1,200 with maleic anhydride. A mixture of 813 grams of the polypropylene-substituted succinic anhydride, 50 grams of a commercial ethylene amine mixture having an average composition corresponding to that of tetraethylene pentamine and 566 grams of mineral oil is heated at 150° C. for 5 hours. The residue is found to have a nitrogen content of 1.18 percent.

#### EXAMPLE 6

A methyl ester of a high molecular weight monocarboxylic acid is prepared by heating an equi-molar mixture of a chlorinated polyisobutene having a molecular weight of 1,000 and a chlorine content of 4.7 percent by weight and methyl methacrylate at 140°-220° C. The resulting ester is then heated with a stoichiometrically equivalent amount of triethylene tetramine at 100°-200° C. to produce an acylated nitrogen compound.

#### EXAMPLE 7

A mixture of 2000 grams of mineral oil, 3 equivalents of trimethylene diamine and 3 equivalents of a high molecular weight tricarboxylic acid prepared by the reaction of a brominated poly (1-hexene) having a molecular weight of 2,000 and a bromine content of 4 percent by weight of 2-pentene-1,3,5-tricarboxylic acid (prepared by dehydration of citric acid) is heated at 150° C. for 20 hours. The residue is filtered to give a homogeneous mineral oil solution of the acylated nitrogen product.

#### EXAMPLE 8

A product is obtained by the procedure of example 1, except that tripentylene tetramine (3 equivalents) is used in lieu of the ethylene diamine.

#### EXAMPLE 9

A mixture of 386 grams of mineral oil, 528 grams of the polyisobutene-substituted succinic anhydride of example 1, and 59 grams of N-(2-hydroxyethyl)-trimethylene-diamine was prepared at 60° C. The mixture was blown with nitrogen at 150°-155° C. for 5 hours. The residue had a nitrogen content of 1.56 percent.

#### EXAMPLE 10

To a mixture of 800 grams of the polyisobutene-substituted succinic anhydride of Example 1 and 175 grams of toluene there was added 77 grams of a commercial mixture of alkylene amines and hydroxy alkyl-substituted alkylene amines consisting of approximately 2 percent (by weight) of diethylene triamine, 36 percent of 1-(2-aminoethyl)piperazine, 11 percent of 1-(2-hydroxy-ethyl)piperazine, 11 percent of N-(2-hydroxyethyl)ethylenediamine, and 40 percent of higher homologues obtained as a result of condensation of the above-indicated amine components. The resulting mixture was heated at the reflux temperature for 16.5 hours whereupon 12 cc. of water was collected as the distillate. The residue was then heated to 160° C./25 mm. and diluted with 570 grams of mineral oil. The final product was found to have a nitrogen content of 1.57 percent.

#### EXAMPLE 11

A substituted monocarboxylic acid acylating agent is obtained by reacting acrylic acid (1 equivalent) with a chlorinated polyisobutene (1 equivalent) having a chlorine content of 4.5 percent and a molecular weight of 850 at 150°-200° C. The product of the reaction is then mixed with 1.25 equivalents of pentaethylene hexamine at 50°-75° C. and the resulting mixture is heated at 180°-200° C. to form an acylated polyamine.

#### EXAMPLE 12

The procedure of Example 11 is repeated except that the acrylic acid is replaced on a chemically equivalent basis with alpha-chloroacrylic acid and the pentaethylene hexamine is replaced on a nitrogen basis with ethylene diamine.

Fuel compositions contemplated by the present invention are illustrated by the following:

#### COMPOSITION A

Gasoline containing 0.1 percent by weight of an additive solution of the present invention, said solution consisting essentially of about 50 percent by weight xylene, 25 percent by weight of a filtrate prepared according to Example 2 wherein the filtrate has a mineral oil content of about 40 percent by weight, and about 25 percent of the acetic acid ester of ethylene glycol mono-n-butylether.

#### COMPOSITION B

Diesel fuel containing 0.5% of the filtrate of Example 7 adjusted to an oil content of 40 percent and 0.75 percent of the 2-ethylhexanoic acid ester dipropylene glycol monomethyl ether.

#### COMPOSITION C

Gasoline containing 1.5 percent of a filtrate prepared from the product of Example 1 and adjusted to an oil content of 40 percent and 2 percent of the methacrylic acid ester of triethylene glycol monopropyl ether.

#### COMPOSITION D

Gasoline containing 0.05 percent of a solution consisting essentially of about 50 percent by weight of xylene, about 25 percent by weight of a filtrate prepared according to the procedure of Example 8 and adjusted to an oil content of 40 percent, about 10 percent by weight of the acetic acid ester of ethylene glycol monophenyl ether, and about 15 percent by weight of the butyric acid ester ethylene glycol mono-n-butyl ether.

By substituting other dispersants and other oxy compounds of the type described hereinbefore for those in the above examples other fuel compositions of the type contemplated by the present invention are readily prepared. The solutions of the additive combinations of this invention which can be used directly as cleaning compositions are illustrated by those used in the preparation of the fuel compositions of Composition A and D above. Similarly, by substituting other solvents of the type described hereinbefore for all or part of the xylene, other cleaning compositions can be readily prepared.

The additive combination of the present invention are particularly valuable since they coact synergistically in the cleaning of the fuel systems. This synergistic effect is illustrated by the following procedure:

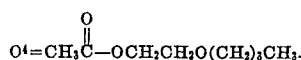
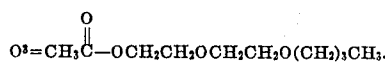
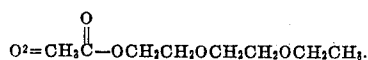
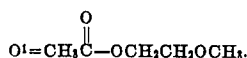
A clean steel test panel (5 7/8 in. × 1 5/16 in. × 1/16 in.) is immersed in a "varnish" solution (prepared by adding 2 percent by weight Enarco sludge to a solution of a 1:1 weight ratio of benzene and acetone) and is allowed to dry thoroughly. This is done three times. Then the prepared panel is used to stir 100 ml. of the test solution in a 250 ml. beaker for five minutes. The amount of deposited sludge removed is rated visually and indicates the effectiveness of the test solu-

tion. Test results of the additive combinations of this invention are tabulated below.

TABLE I

Test composition number	Mineral oil	Components		Oxy compound	Concentration (ml.)	Percent sludge removed
		Xylene	Dispersant			
1	X	X			40:50	0-5
2	X	X	D <sup>1</sup>		40:50:10	30-35
3	X	X		O <sup>1</sup>	40:50:10	2-7
4	X	X	D <sup>1</sup>	O <sup>1</sup>	40:50:5:5	80-90
5	X	X		O <sup>2</sup>	40:50:10	0-5
6	X	X	D <sup>1</sup>	O <sup>2</sup>	40:50:5:5	90-100
7	X	X		O <sup>3</sup>	40:50:10	0-5
8	X	X	D <sup>1</sup>	O <sup>3</sup>	40:50:10	85-95
9	X	X		O <sup>4</sup>	40:50:10	2-7
10	X	X	D <sup>1</sup>	O <sup>4</sup>	40:50:5:5	95-100

D<sup>1</sup> Mineral oil solution (30% by weight oil) of a commercially available ashless dispersant prepared by reacting polyisobutenyl (average mol. wt. 850-1,100)-substituted succinic anhydride and an ethylene polyamine mixture having an average of about five amino groups per molecule in an equivalent ratio of anhydride to polyamine of about 1:1.1 according to the general procedures described and illustrated in U.S. patent 3,172,892.



From the foregoing test, it is clear that the combination of additives provides an amount of sludge reduction which is greatly in excess of that of either additive alone or the cumulative sludge reduction of both additives.

As will be apparent to those skilled in the art, the fuels used in the fuel compositions will normally be petroleum distillate fuels, such as fuel oils, diesel fuels, kerosene, gasolines, aviation fuels, etc. Furthermore, the fuel compositions of this invention may contain other conventional additives such as smoke suppressants, alkyl lead antiknock agents, antistatic agents, corrosion inhibitors, antioxidants, antiicing agents, lead scavengers, lead octane appreciators, dyes, and the like.

What is claimed is:

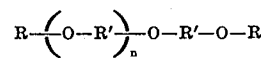
1. A liquid fuel composition comprising a major amount of at least one normally liquid fuel and a minor amount sufficient for inhibiting and removing sludge and other deposits which accumulate in fuel systems, of an additive combination soluble in said fuel, the additive combination comprising at least one oxy compound selected from the class consisting of glycols, polyglycols, and the carboxylic acid esters of these glycols, polyglycols, and monoethers thereof with monocarboxylic acids containing up to about 20 carbon atoms, and at least one fuel-soluble ashless dispersant selected from the class consisting of esters, amides, imides, amidines, and amine salts of at least one substantially saturated carboxylic acid characterized by the presence within its structure of at least about 30 aliphatic carbon atoms; the weight ratio of oxy compound to dispersant being about 1:10 to about 10:1.

2. A fuel composition according to claim 1 wherein said dispersant is an acylated nitrogen composition characterized by the presence within its structure of a substantially saturated hydrocarbon-substituted polar group selected from the class consisting of acyl, acylimido, and acyloxy radicals wherein the substantially saturated hydrocarbon substituent contains at least about thirty aliphatic carbon atoms and a nitrogen-containing group characterized by a nitrogen atom attached directly to said polar radical.

3. A fuel composition according to claim 1 containing from about 0.001 to about 5 percent by weight of said additive combination wherein the dispersant is at least one ester, amide,

imide amidine, or amine salt of a polymerized olefin-substituted mono- or dicarboxylic acid or a chlorinated, polymerized olefin-substituted mono- or dicarboxylic acid containing at least about thirty aliphatic carbon atoms in the carboxylic acid moiety.

4. A fuel composition according to claim 3 where said at least one oxy compound corresponds to those represented by the formula:



where n is such that the average molecular weight of the oxy compound is not greater than about 1,500, each R is independently selected from the class consisting of H, hydrocarbyl of up to about eight carbon atoms, or a monocarboxylic acid acyl radical of up to about twenty carbon atoms, with the proviso that at least one R variable is an acyl radical and R' is hydrocarbylene of up to about eight carbon atoms.

5. A gasoline fuel composition according to claim 4 where n is 0, 1, 2, or 3, each R is independently H, phenyl, alkyl phenyl, or alkyl with the proviso that at least one R variable is an acyl radical of an aliphatic monocarboxylic acid.

6. A gasoline fuel composition according to claim 5 wherein the dispersant is the reaction product of at least one of said substituted mono- or dicarboxylic acids or their anhydrides and at least one alkylene polyamine having up to about ten amino nitrogen atoms where the ratio of substituted mono- or dicarboxylic acid or anhydride and the alkylene polyamine in the reaction mixture is from about one equivalent of acid or anhydride per equivalent of alkylene polyamine to about one equivalent of acid or anhydride per mole of alkylene polyamine.

7. A gasoline fuel composition according to claim 6 wherein one R is lower alkyl and the other R is a lower alkanoyl radical.

8. A gasoline fuel composition according to claim 7 wherein the dispersant is the reaction product of at least one polyisobutenyl substituted-succinic acid or anhydride or a chlorinated polyisobutenyl substituted-succinic acid or anhydride and at least one ethylene polyamine having from two to six amino nitrogen atoms in the molecules thereof, wherein the polyisobutenyl-substituted succinic acid or anhydride and the ethylene polyamine are reacted in an equivalent ratio of about 1:1 to about 1:3.

9. A gasoline fuel composition according to claim 8 wherein the oxy compound is the acetic acid ester of ethylene glycol monobutyl ether.

10. A fuel composition according to claim 1 wherein the normally liquid fuel is a petroleum distillate fuel.

11. A fuel composition according to claim 10 wherein the normally liquid fuel is a petroleum distillate fuel boiling in the gasoline range.

12. A fuel composition according to claim 1 wherein said additive combination contains at least one substantially inert organic solvent for the said additive combination.

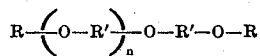
13. A fuel composition according to claim 12 wherein the solvent is an aromatic hydrocarbon.

14. A composition useful in the method for cleaning the fuel system of a liquid fuel burning internal combustion engine or liquid fuel burning heating device comprising contacting at least the internal surfaces of said fuel system with a cleaning composition, said composition comprising a solution of (1) at least one oxy compound selected from the class consisting of glycols, polyglycols, and the carboxylic acid esters of these glycols, polyglycols, and monoethers thereof with monocarboxylic acids containing up to about twenty carbon atoms and (2) at least one fuel-soluble ashless dispersant selected from the class consisting of esters, amides, imides, amidines, and amine salts of at least one substantially saturated carboxylic acid characterized by the presence within its structure of at least about thirty aliphatic carbon atoms, wherein the weight ratio of oxy compound to dispersant being about 1:10 to about 10:1, and (3) a solvent for the combination of (1) and (2)



wherein the solvent for the combination of (1) and (2) is at least one normally liquid, substantially inert, organic compound, the total amount of the combination of (1) and (2) being from about 5 to about 70 percent by weight of the total weight of composition.

15. The composition according to claim 14 wherein the oxy compounds correspond to the formula



where n is such that the average molecular weight of the oxy compounds is not greater than about 1,500, each R is independently selected from H, hydrocarbyl of up to about twelve carbon atoms, or a monocarboxylic acid acyl radical of up to about twenty carbon atoms with the proviso that at least one R variable is an acyl radical, and R' is hydrocarbylene of up to about eight carbon atoms; and wherein the dispersant is the reaction product of at least one acylating agent selected from the class consisting of polymerized olefin-substituted mono- or dicarboxylic acid or chlorinated polymerized olefin-substituted mono- or dicarboxylic acid, or the lower alkyl esters, acyl halides, or anhydrides, of those containing at least about thirty aliphatic carbon atoms in the carboxylic acid moiety with at least one alkylene polyamine having up to about ten amino nitrogen atoms wherein the ratio of acylating agent to alkylene polyamine in the reaction mixture is from about one equivalent of acylating agent per equivalent of alkylene

polyamines to about one equivalent of acylating agent to about one mole of alkylene polyamine; and wherein the solvent is a normally liquid aromatic hydrocarbon.

16. A composition according to claim 15 wherein n is 0, 1, 2, or 3, each R is independently H, hydrocarbyl of up to about eight carbon atoms, or a monocarboxylic acid acyl radical of up to about twelve carbon atoms, with the proviso that at least one R variable is an aliphatic monocarboxylic acid acyl radical, and R' is alkylene of up to about eight carbon atoms and wherein the dispersant is the reaction product obtained by reacting at least one polyisobutenyl-substituted or chlorinated polyisobutenyl-substituted succinic acid or anhydride with an ethylene polyamine.

17. A composition according to claim 16 wherein one R is alkyl and the other is lower alkanoyl and the dispersant is the reaction product of at least one polyisobutenyl-substituted or chlorinated polyisobutenyl-substituted succinic acid or anhydride and an ethylene polyamine having from two to six amino nitrogen atoms in the molecules thereof wherein the succinic acid or anhydride and the ethylene polyamine are reacted in an equivalent ratio of about 1:1 to about 1:3, and wherein the solvent is at least one alkyl-substituted benzene containing up to 12 carbon atoms.

18. The method according to claim 17 wherein oxy compound is the acetic acid ester of ethylene glycol monobutyl ether.

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UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 3,658,495 Dated April 25, 1972

Inventor(s) Casper J. Dorer, Jr.

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

Column 14, line 24, claim 18, "The method according" should read --The composition according--.

Signed and sealed this 26th day of December 1972.

(SEAL)  
Attest:

EDWARD M. FLETCHER, JR.  
Attesting Officer

ROBERT GOTTSCHALK  
Commissioner of Patents