

[54] **FUEL COMPOSITIONS COMPRISING A COMBINATION OF MONOETHER AND ASHLESS DISPERSANTS**

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

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[57]

ABSTRACT

Fuel compositions containing an additive combination comprising an oxy compound and a dispersant. The oxy compounds are the 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 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 MONOETHER 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 the 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.

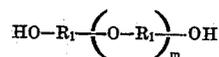
A still further object of this invention is to provide methods for cleaning the fuel systems of internal combustion engines and other liquid-fuel burning devices through the use of the additive combination of this invention.

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 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 the monoethers of glycols and polyglycols 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 0.1:1 to about 1:0.1 but preferably 0.1:1 to about 2.5:1. 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. One of the attributes of the additive combination is that the dispersants promote 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 in order to achieve solubility of an additive combination for a given fuel composition.

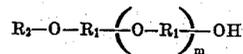
The term "glycol" as used in the present specification and claims is intended to describe dihydric organic compounds of the formula $\text{HO}-\text{R}_1-\text{OH}$ wherein R_1 is a divalent hydrocarbon or substituted hydrocarbon radical. Thus, R_1 can be alkylene, phenylene, cyclohexylene, or a substituted variation 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-chlorophenylene-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 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



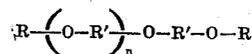
where each R_1 is independently a divalent radical of the type described above and m is at least 1.

The oxy compounds contemplated by the present invention are the monoethers of these glycols and polyglycols. These monoethers can be represented by formula $\text{R}_2-\text{O}-\text{R}_1-\text{OH}$ and



wherein R_2 is a monovalent hydrocarbon or substituted hydrocarbon radical and R_1 and m are as defined above. Thus, 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 R_1 . R_2 normally will contain up to about 12 carbon atoms. R_2 will usually be a hydrocarbon radical, particularly an alkyl radical, a phenyl radical, an alkyl phenyl radical, a phenyl alkyl radical, or an alkylphenyl alkyl radical. Illustrative examples of R_2 include methyl, ethyl, propyl, isopropyl, butyl, tertiary butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, phenyl, benzyl, p-ethylbenzyl, tolyl, xylyl, phenethyl, p-methoxyphenyl, cyclohexyl, cyclopentyl, p-(tert-butyl)phenyl and the like.

A particularly preferred class of oxy compounds can be represented by 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 the class consisting of hydrogen and hydrocarbyl of up to about eight carbon atoms with the proviso that both R variables are not hydrocarbyl, and R' is hydrocarbylene of up to about eight carbon atoms. Where both R variables are hydrocarbyl, the oxy compounds are not effective in the additive combination of this invention. The hydrocarbyl groups may be aliphatic, cycloaliphatic or aromatic and the hydrocarbylene groups may be aliphatic, cycloaliphatic or aromatic groups. Preferably however, the hydrocarbylene groups will be aliphatic. 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 , phenyl, alkylphenyl, alkylphenylalkyl, or alkyl with the proviso that at least one R variable is H and R' is alkylene.

Examples of oxy compounds are the monoethers of 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. Specific examples include ethylene glycol monophenyl ether, ethylene glycol monomethylether, ethylene glycol monoethyl ether, ethylene glycol mono-(n-butyl)ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol mono-(n-butyl)ether, propylene glycol monomethyl ether, dipropylene glycol monomethyl ether, diethylene glycol monocyclohexylether, ethylene glycol monobenzyl ether, triethylene glycol monophenethyl ether, butylene glycol mono(p-(n-butoxy)phenyl)ether, trimethylene glycol mono(alkylphenyl)ether, tripropylene glycol monomethyl ether, ethylene glycol monoisopropylether, ethylene glycol monoisobutylether, ethylene glycol monohex-

yl ether, triethylene glycol monobutyl ether, triethylene glycol monomethyl ether, triethylene glycol monoethyl ether, 1-butoxyethoxy-2-propanol, monophenyl ether of polypropylene glycol having an average molecular weight of about 975-1,075, and 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 975-1,075. Such oxy compounds are sold in commerce under such names as Butyl CELLOSOLVE, Ethyl CELLOSOLVE, Hexyl Cellosolve, Methyl CARBITOL, Butyl CARBITOL, DOWANOL Glycol ethers, and the like. Such compounds are also disclosed in U.S. Pats. 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, 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 30 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 patents: 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 1,055,337. 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 an 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 α,β -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, acrotonic 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 α,β -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 unsaturated 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 3,000 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 inter-

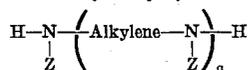
mediates in the synthesis of the dispersants are disclosed in the above-incorporated patents.

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 40 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-methyl-octyl 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



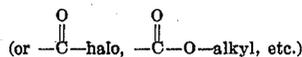
where q is an integer of 1-9 and Z is lower alkyl or H in a ratio of acylating agent to alkylene polyamine of one equivalent of acylating agent to one equivalent of alkylene polyamine to about one equivalent of acylating agent to one mole of alkylene polyamine. The reaction is generally conducted by 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-aminoethylpiperazine, 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.

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 anhydride 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 pres-

sure 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 63.6 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 1,056 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°-190° C.) for 5 hours. A total of 18 grams of water is collected 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 1200 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 2,000 grams of mineral oil, 3 equivalents of trimethylene diamine and three 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 tripropylene 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% of 1-(2-hydroxyethyl)piperazine, 11 percent of N-(2-hydroxyethyl)ethylenediamine, and 40% 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 ethylene glycol mono-n-butylether.

COMPOSITION B

Diesel fuel containing 0.5 percent of the filtrate of Example 7 adjusted to an oil content of 40 percent and 0.75 percent of 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 triethylene glycol monoethyl 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 ethylene glycol monophenyl ether, and about 15 percent by weight of ethylene glycol mono-n-butyl ether.

By substituting other dispersants and other oxy compounds of the type described hereinabove for those in the above examples other fuel compositions of the type contemplated by the present invention are readily prepared. The solution of the additive combination of this invention which can be used 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:

SAE 1020 steel panels (1½ inches by 6 inches) are cleaned with xylene, weighed and hung fully immersed in a borosilicate test tube containing 350 milliliters of mineral oil. A tube is placed into a heated block and heated to 300° F. while air is introduced into the oil by means of a coarse fritted glass cylinder at a rate of 10 liters per hour. The panels are then removed from the oil after 48 hours, rinsed thoroughly with naphtha, dried, and weighed to determine the amount of sludge on the panel. These weighed panels are then fully immersed into a 500 milliliter flask containing 300 milliliters of test fluid. While the panel is immersed in the test fluid, the fluid is stirred with a magnetic stirring bar for two hours at room temperature. This panel is then removed from the test fluid, rinsed thoroughly with naphtha, dried in an oven at 100° C. for 15 minutes and weighed to determine the amount of sludge remaining on the panel. The ratio of sludge lost from the panel after the test compared with the initial amount of sludge on the panel is reported as percent sludge reduction. Table I below records the results of such test.

TABLE I

Test Fluid Composition	Panel No.	Milligrams of Sludge on Panel		Percent Sludge Reduction
		Beginning of Test	End of Test	
(1)	1-H	9.3	9.2	1.1
(2)	1-N	8.0	8.6	7.5 (increase)
(3)	1-I	7.5	4.0	46.7
(4)	1-M	7.7	1.2	84.4
(5)	1-F	10.2	10.2	0
(6)	1-E	12.1	11.9	1.7
(7)	1-B	17.1	8.9	48.0
(8)	1-P	17.8	4.0	77.5

(1), (5) — Mineral oil only.

(2), (6) — Mineral oil and filtrate of reaction product of polyisobutenyl (M.W. 1000) — substituted succinic anhydride and an ethylene polyamine mixture containing from two to six amino groups per molecule prepared according to the procedure of Example 1 and where the amount of oil in the filtrate is adjusted to 40 percent. The weight ratio of mineral oil to filtrate is 12:1.

(3), (7) — Mineral oil and ethylene glycol mono-n-butyl ether in a weight ratio of 12:7.

(4), (8) — Mineral oil, ether of (3) and (7), and filtrate of (2) and (6) in a weight ratio of 12:7:1.

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. Another test demonstrates that the synergistic effect also exists when the additive combination comprises a basic dispersant. This test is conducted according to the following procedure:

Steel test panels (5.875 inches by 1.313 inches by 0.0625 inches) are prepared by dipping them into a varnish solution three times. The solution is allowed to dry on the panel after each immersion. The varnished solution into which the panels are immersed is prepared by adding 2 percent weight of sludge to an equal volume solution of benzene and acetone. Thereafter a beaker containing 100 milliliters of the solution to be evaluated is stirred with the test panel for 5 minutes. After this stirring the panels are rated visually to ascertain the extent of varnish reduction. The results of such a test are recorded in Table II below.

TABLE II

Test Fluid Composition	Percent Varnish Removed
Xylene and Mineral oil in a Volume Ratio of 40:50	1-2
Xylene, Mineral Oil and Dispersant ^a in a Volume Ratio of 40:50:10	5-10
Xylene, Mineral oil, and Oxy Compound ^b in a volume Ratio of 40:50:10	1-2
Xylene, Mineral oil, Dispersant ^a , and Oxy Compound ^b in a Volume Ratio of 40:50:5:5	98-99

a — A 40 percent oil solution of the filtered reaction product of polyisobutenyl (M.W. — 1000) — substituted succinic anhydride and an ethylene polyamine mixture prepared according to the procedure of Example 1 using an equivalent ratio of anhydride to ethylene polyamine to about 1:1.3.

b — Ethylene glycol mono-n-butyl ether.

Again, it is apparent that the additive combination is far more effective in the reduction of varnish than either of the components of the combination alone.

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.

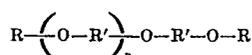
What is claimed is:

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 which is a monoether of a glycol or polyglycol 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 thirty aliphatic carbon atoms; the weight ratio of oxy compound to dispersant being about 0.1:1 to about 2.5:1.

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, amidines 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 and hydrocarbyl of up to about eight carbon atoms with the proviso that both R variables are not hydrocarbyl, 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, phenylalkyl, alkylphenylalkyl, or alkyl with the proviso that at least one R variable is H, and R' is alkylene.

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 n is 0, one R is H, and the other R is alkyl.

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 ethylene glycol monobutyl ether.

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

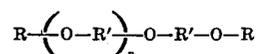
11. A fuel composition according to claim 10 wherein the normally liquid fuel is a petroleum distillate fuel boiling in the gasoline range.

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 which is a monoether of a glycol or polyglycol 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, the weight ratio of oxy compound to dispersant being about 0.1:1 to about 2.5:1 and (3) a solvent for the combination of (1) and (2) wherein (3) 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 and hydrocarbyl of up to about 12 carbon atoms with the proviso that both R variables are not

hydrocarbyl, 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 30 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 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 or alkyl of up to about eight carbon atoms, with the proviso that both R variables are not

alkyl and R' is alkylene of up to about eight carbon atoms and wherein the dispersant is the reaction product obtained by reacting at least polyisobutenyl-substituted or chlorinated polyisobutenyl-substituted succinic acid or anhydride with an ethylene polyamine.

17. A composition according to claim 16 wherein the n is 0, one R is H, and the other is lower alkyl 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 composition according to claim 17 wherein oxy compound is ethylene glycol monobutyl ether.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,658,494 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:

At column 14, line 3, that is Claim 16, line 6,
"at least polyisobutenyl-substituted" should be
--at least one polyisobutenyl-substituted--.

Signed and sealed this 29th day of August 1972.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents