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[54] **MULTI-FUNCTIONAL FUEL ADDITIVE COMPOSITIONS**

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[52] **U.S. Cl.** **44/58;** 44/DIG. 1

[51] **Int. Cl.** **C10l 1/18**

[58] **Field of Search** 44/DIG. 1, 62, 80, 58

[56] **References Cited**

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[57] **ABSTRACT**

Combinations of (A) polymers of C_3–C_4 olefins having a molecular weight in the range of about 400 to about 1400; and (B) polyoxyalkylene compounds of the formula

$$R(OCH_2\underset{\displaystyle CH_3}{\underset{|}{CH}})_xOH$$

wherein R is an alkyl group of 1 to 20 carbon atoms and wherein x has an average value of 4 to 20; are effective as anti-icing additives, as carburetor detergents and in some instances as intake valve deposit modifiers.

4 Claims, No Drawings

MULTI-FUNCTIONAL FUEL ADDITIVE COMPOSITIONS

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to multi-functional fuel additives, and more particularly is directed to the additive compositions comprising a C_3–C_4 olefin polymer and a polyoxyalkylene compound, which in fuels are effective as anti-icers, as carburetor detergents, and in some instances, as intake valve deposit modifiers.

2. Prior Art

In the operation of internal combustion engines in automotive, marine, aircraft and stationary use various operational difficulties have been encountered. These include icing, which generally occurs in cool humid atmospheric conditions; accumulation of deposits in the carburetor; and accumulation of deposits on the intake valves and ports. Various additives have been used to combat these difficulties with varying degrees of success. Anti-icing additives have included polyoxyalkylene ethers (see British Pat. No. 709,987); additives to reduce carburetor deposits have included amine esters of alkyl phosphates; and additives to remove valve deposits have included polymers of C_3 to C_4 olefins (See U.S. Pat. No. 3,502,451).

It is particularly desirable to reduce more than one such operational difficulty with a single additive or with an additive that is a combination of two or more compounds. It is an object of this invention to provide an additive composition, for use in liquid hydrocarbon fuels, which will function simultaneously as an anti-icing agent, a carburetor detergent and an intake valve deposit reducer. It is a further object of this invention to provide a multi-functional fuel additive which contains only the elements carbon, hydrogen and oxygen. These and other objectives are achieved by the compositions described hereinbelow.

SUMMARY

In summary, this invention is directed to a multi-functional fuel additive composition consisting essentially of

A. a polymer of a 3- or 4- carbon olefin having a molecular weight of from about 400 to about 1400, and

B. from about 10 to about 160 percent by weight of said polymer of a polyoxyalkylene compound of the formula

$$R(OCH_2\overset{\overset{CH_3}{|}}{C}H)_xOH$$

wherein R is alkyl of 1 to 20 carbon atoms, and x has an average value of 4 to 20.

The additive compositions of this invention impart to hydrocarbon fuels the desirable combined effect of anti-icing and carburetor detergency and through the most preferred embodiments of this invention the additional benefit of reduced intake valve deposits.

DESCRIPTION OF THE INVENTION

As stated above, this invention is directed to a liquid hydrocarbon fuel additive consisting essentially of an olefin polymer and a polyoxyalkylene compound. The additive components, their relative concentrations in the additive composition and the ultimate fuel compositions, and methods of preparing such compositions are described below.

1. Components

A. Hydrocarbon polymers

The hydrocarbon polymers of the composition of the invention are those prepared from C_3 to C_4 olefins. The hydrocarbon polymers thus comprise polypropylene, polybutylenes and copolymers of propylene and butylenes. The hydrocarbon polymers should have a molecular weight in the range of about 400 to about 1400 and are thus liquids at ordinary temperatures and have viscosities in the range of about 500 SUS to about 125,000 SUS at 100°F. The molecular weights of the hydrocarbon polymers are number average molecular weights as determined by vapor pressure osmometry according to ASTM D2503 while the viscosities are determined according to ASTM D–445. The preferred hydrocarbon polymers of this invention are those with a molecular weight of less than 900 and the most preferred polymer of the invention is polyisobutylene, that is, a hydrocarbon polymer having the structural unit represented by $—C(CH_3)_2CH_2—$ as the principal chain unit. The hydrocarbon polymers useful in the invention are readily prepared by the known polymerization methods of the art. The useful polymers can also be prepared by cracking higher molecular weight polypropylenes or propylene-butylene copolymers to the above-described molecular weight range. As will be apparent to those skilled in the art, a mixture of hydrocarbon polymers such as polypropylenes and polybutylenes having the above defined molecular weight range can also be used in the additives of this invention. The preferred polyisobutylenes in the desired molecular weight range are available commercially.

B. Polyoxyalkylenes

The polyoxyalkylene compounds of the additives of this invention are represented by the formula

$$R(OCH_2\overset{\overset{CH_3}{|}}{C}H)_xOH$$

wherein R is an alkyl group of 1 to 20 carbon atoms and x is from about 4 to about 20. Thus the polyoxyalkylene compound is a monoalkyl ether of polyoxypropylene glycol. The radical R can be any alkyl group of 1 to 20 carbon atoms and includes methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosanyl as well as the various isomeric forms of such radicals. The monoalkyl ethers of polyoxypropylene glycol such as those of methyl, ethyl, propyl and butyl are commercially available, while the remainder of the monoalkyl ethers are readily prepared by the well known methods of the art according to the equation:

$$ROH + x\overset{\overset{O}{\diagup\ \diagdown}}{CH_2—CH}—CH_3 \xrightarrow[\text{catalyst}]{\text{alkaline}} R(OCH_2\overset{\overset{CH_3}{|}}{C}H)_xOH$$

wherein ROH represents an alcohol with the desired R group and x represents the number of moles of 1,2-propylene oxide per mole of the alcohol.

The monoalkyl ether of polyoxypropylene glycol of the invention can be a single compound or can be a mixture containing different alkyl groups. Particularly useful and preferred compounds are prepared from a mixture of C_{12} to C_{16} straight chain alcohols, the resulting alkyl ethers being a mixture of normal C_{12} to C_{16} alkyl ethers of polyoxypropylene glycol. The C_{12} to C_{16} alcohol mixture is readily and economically available by a reaction involving telomerization of ethylene and is sold under the tradename "Alfol" by Continental Oil Company. The number of propylene oxide units in the compound is readily controlled by the adjustment of the propylene oxide-alcohol ratio in the above equation. As is generally recognized the above reactions of propylene oxide with an alcohol and the reaction of propylene oxide to form polyoxypropylene glycol are polymerization processes and as such, the products obtained are mixtures of compounds with different number of propylene oxide units present. In the polyoxyalkylene compound of the formula

$$R(OCH_2\underset{\displaystyle CH_3}{\underset{|}{C}}H)_xOH,$$

the value of x represents an average number of oxyalkylene units in the compound. The polyoxyalkylene compounds of this invention thus have average values of x in the range of about 4 to about 20. The preferred polyoxyalkylene compounds of the formula

$$R(OCH_2\underset{\displaystyle CH_3}{\underset{|}{C}}H)_xOH$$

have R which is an alkyl group of from 10 to 18 carbon atoms and x in the range of 5 to 10. The most preferred polyoxyalkylene compound is that wherein the R group is a mixture of alkyl groups of 12 to 16 carbon atoms and x has an average value of 7.

C. The additive composition

The two components of the additive composition are usually present in such amounts that for each 100 parts of the hydrocarbon polymer there is present from about 10 parts to about 160 parts of the polyoxyalkylene compound. The two components of the combination of the invention can be added separately to the fuel or they can be added together either as a mixture of the two components or as a concentrate in a suitable carrier such as liquid hydrocarbon. When solvents are used to facilitate handling and mixing, any desired amount of the solvent can be used. Generally, however, the amount of solvent used in the range of up to 90 percent of the composition. For convenience in handling, the solution should contain from about 10 to 40 percent, more preferably about 10 to 30 percent by weight of the solvent. Suitable solvents are those boiling in the gasoline range and include pentane, hexane, cyclohexane, isooctane, kerosene, benzene, toluene, xylenes and the like. The preferred solvent is the commercial mixed xylene.

It has surprisingly been found that a combination of the hydrocarbon polymer as defined and the preferred polyoxyalkylene compound, that is a compound of the formula

$$R(OCH_2\underset{\displaystyle CH_3}{\underset{|}{C}}H)_xOH$$

wherein R is a mixture of alkyl groups of 10 to 18 carbon atoms and wherein x has an average value of 5 to 10, form homogeneous solutions when mixed. Thus when 80 parts of polyisobutylene of 800 molecular weight or when 80 parts of polypropylene of 840 molecular weight is combined with 20 parts of the preferred polyoxyalkylene compounds wherein R and x are as defined, at room temperature, a compatible homogeneous solution is obtained. It is generally recognized in the art of polymer science that when two dissimilar polymers are mixed, incompatibility is usually to be expected. The beneficial effects of the compatibility of the components of the combination of the present invention are (1) upon storage at ambient temperatures no separation of the components takes place and thus no precaution is necessary to insure that the addition of the components in the proper proportion will take place after a period of storage — this is particularly important when only a portion of the additive is to be added to the fuel; and (2) cost of storage and shipping is minimized since only the active additive is handled. Even more surprising, it has been found that these selected compositions which form homogeneous solutions are also highly effective in preventing intake valve deposit build-up when used in hydrocarbon fuels.

The additives of this invention are used by incorporating them into fuels such as hydrocarbons boiling in the gasoline boiling range. The base fuel can consist of straight chain or branched chain paraffins, cycloparaffins, olefins, and aromatic compounds or any mixture of these, such hydrocarbons being obtainable from straight run naphtha, polymer gasoline, natural gasoline, thermally or catalytically cracked hydrocarbons and catalytically reformed stocks. Normally the hydrocarbon polymer is added in amounts ranging from about 0.01 to about 0.06 weight percent and the polyoxyalkylene from about 0.004 to 0.016 weight percent, both based on the weight of fuel.

The hydrocarbon fuel can also contain any of the conventional additives such as anti-knock compounds which include tetraethyl lead, tetramethyl lead and tetraalkyl lead wherein the alkyl groups are a mixture of methyl and ethyl groups; halogen containing lead scavenging compounds such as ethylene chloride, ethylene bromide or a mixture thereof; and other conventional additives such as corrosion inhibitors, dyes, antioxidants, anti-rust agents, anti-icing agents, inhibitors of gum formation, anti-preignition agents and the like.

EXAMPLE 1

This example illustrates the preparation of R_{12-16}

$$(OCH_2\underset{\displaystyle CH_3}{\underset{|}{C}}H)_7OH.$$

The alcohol used was a mixture of primary straight chain alcohols produced by the reaction of telomerization of ethylene, which is sold under the tradename of "Alfol" by Continental Oil Company. Typically the mixture has the following composition:

1% $C_{10}H_{21}OH$
61% $C_{12}H_{25}OH$
26% $C_{14}H_{29}OH$
11% $C_{16}H_{33}OH$
1% $C_{18}H_{37}OH$

For convenience, since the amount of C_{10} and C_{18} alcohol is negligible, the above alcohol mixture will be referred to as C_{12}–C_{16} alcohol.

To a clean dry autoclave of 600 cubic centimeters capacity, 200 grams of C_{12}–C_{16} alcohol and 0.5 gram of sodium hydride are added. The autoclave is closed, pressurized with dry nitrogen and then vented. Pressurization and venting with nitrogen is repeated four times. With the pressure in the autoclave at atmospheric pressure, the closed autoclave is then heated to 145°–150°C. Any build-up in pressure is relieved by venting to keep the pressure at 10–20 pounds. With the autoclave temperature at 145°–150°C., propylene oxide is added to the autoclave to increase the pressure to about 80 pounds. As the reaction proceeds the pressure will decrease to about 20 pounds. The addition of propylene oxide to 80 pounds followed by the pressure drop to 20 pounds is repeated until a total of 410 grams of propylene oxide have been added, the autoclave is maintained at 145°–150°C. for one-half hour. The autoclave is then allowed to cool to room temperature and the catalyst is neutralized by adding the required amount of concentrated sulfuric acid. The product obtained is a clear, somewhat viscous liquid having a cloud point of less than 0°F. If desired, this product can be filtered for clarification.

EXAMPLE 2

The additive combination of the present invention shows unexpected effectiveness in cleaning deposits formed in a carburetor. In a detergency test described below, deposits are initially accumulated in the carburetor under specified conditions. The effectiveness of an additive as a carburetor detergent is then determined by operating the engine with a fuel containing the additive and then determining the amount of accumulated deposits which are removed. The fuel used in the carburetor detergency test had the following inspection data:

A.P.I.° gravity	59.4
Initial b. pt. °F.	96
Recovered, by volume	
5%	114
20%	138
50%	201
70%	259
90%	341
End point	410
Residue, % by volume	1.0
Aromatics, % by vol.	25
Olefins, % by vol.	12
Saturates, % by vol.	63
Sulfur, Wt. %	0.068
Tetraethyl lead, g/gal	2.53*

*includes 0.5 mole ethylenedibromide and 1.0 mole ethylene dichloride per mole of tetraethyl lead

The carburetor detergency test was carried out as follows:

Detergency Test Procedure

A Chevrolet 6 cylinder, 230 cu. in. engine was used having a Carter No. 3511–S carburetor and an ice tower with heater. The ring gap of the top piston ring was increased by ⅛ inch to a gap of 0.138 inch and installed in place of the second compression ring leaving the top ring groove empty thus increasing the blowby. The total engine blowby was directed to the carburetor air cleaner from the dome cover. The air cleaner filter element was eliminated. The exhaust line was modified to supply engine exhaust to the carburetor air cleaner. The distributor vacuum advance was eliminated to maintain spark advance of 4° before top center.

The operating conditions were as follows: engine speed at 700 ± 10 rpm; water outlet temperature 175 ± 2.5°F.; air/fuel mixture set for maximum vacuum; carburetor air was cooled by passage through an ice tower and then reheated to 90°–95°F.; engine exhaust supply to the carburetor air inlet was controlled as indicated below.

A. Deposit Accumulation (control fuel)

New spark plugs were installed, motor oil was changed to an SAE 30 low detergent oil, carburetor, air cleaner housing and exhaust system were cleaned. The engine was started with the exhaust feed valve to engine inlet air closed. The speed was adjusted to 700 rpm at maximum vacuum. The exhaust feed valve was opened and engine speed maintained at 700 rpm. The exhaust feed valve setting is critical. This setting was such as to feed the maximum amount of exhaust that the engine would accept and still operate smoothly without stalling. By this method there is produced in the shortest time sufficient throttle body deposit for the clean-up phase of the test.

The engine was operated for 10 hours or until it could no longer be kept running under these conditions. The carburetor was removed and rated using a visual rating chart. A rating of 100 is clean. If a rating cleaner than 30 was obtained, additional deposit accumulation operation was required.

B. Deposit Cleanup

The engine conditions are the same as those for (A), except that blowby and exhaust are not fed into the air inlet. The cleanup procedure was followed for 50 hours. Ratings were made at each 10 hour interval to determine the amount and speed of cleanup. Per cent cleanup was determined as follows:

1. 100 minus rating of deposit accumulation = amount available for cleanup.
2. rating after cleanup minus rating of accumulation = amount of cleanup.
3. per cent cleanup = amount of cleanup divided by amount available for cleanup multiplied by 100.

For the test appropriate amounts of polypropylene and polyisobutylene were blended into samples of the above fuel to give desired concentrations. Polyoxyalkylene compounds, described below, were then blended into the fuel. The polyoxyalkylene compounds used in this example are identified as follows:

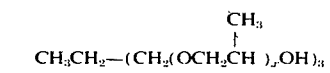
A is the compound prepared in Example 1, which is represented by the general formula

$$R_{12\text{-}16}(OCH_2\underset{\displaystyle CH_3}{\underset{|}{C}}H)_7OH$$

wherein R_{12-16} indicate that the R group is a mixture of alkyl groups of 12 to 16 carbon atoms and 7 represents

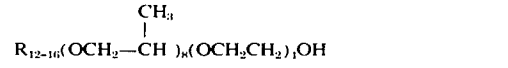
the average number of 1,2-propylene oxide units in the molecule.

B is propoxylated trimethylol propane which can be represented by



and has a molecular weight of 1535, thus indicating an average value for x of 8.2.

C is a compound containing both the 1,2-propylene oxide and ethylene oxide units and is represented by



wherein R_{12-16}, as in A above, indicates the alkyl group is a mixture of alkyl groups of 12 to 16 carbon atoms, and 8 and 4 represent an average number of 1,2-propylene oxide units and ethylene oxide units respectively.

D is ethoxylated isooctyl phenol wherein the compound has an average of 4 ethylene oxide units.

The results of the carburetor detergency tests are summarized in the following Table I. The concentration of the additive components given in the Table is in weight percent based on the fuel. Table I shows that the combination of the polymer and polyoxyalkylene compound A is remarkably effective in removing deposits from dirty carburetors. The results can be seen much more readily from Table II wherein the clean-up data are tabulated in terms of increase in the carburetor clean-up. Since the use of the base fuel by itself results in 16 percent cleanup, any carburetor cleanup value of 16 percent or less in Table I is recorded as 0 increase in Table II while any cleanup value of greater than 16 percent is recorded as the difference between the cleanup value and 16 percent. Thus, by way of illustration, in test No. 1 when polyoxyalkylene compound A is used at 20 pounds per thousand barrels range the cleanup value is 7 percent and is thus recorded in Table II as 0 carburetor cleanup increase while when compound A is used at 40 pounds per thousand barrels range the cleanup value in Table I is 25 percent and is thus recorded in Table II as carburetor cleanup increase of 9 percent. Table II clearly shows that the cleanup effect when polyisobutylene whose molecular weight range is from about 400 to about 900 and when used in the concentration range of from about 0.01 to 0.06 per cent by weight, when used together with polyoxyalkylene compound is considerably greater than that expected from the performance of either the polyisobutylene or polyoxyalkylene compound. Table II also shows: (1) no cleanup is obtained when polyisobutylene is used in higher concentrations (No. 6); and (2) no synergistic cleanup is obtained when the polyoxyalkylene compound is B, C or D.

EXAMPLE 3

This example illustrates the effectiveness of the additive combinations of the invention in preventing intake valve deposits. Motor gasoline having a tendency to form intake valve deposits under ordinary driving conditions was used. The gasoline had the following inspection data:

A.P.I° gravity	58.9
Initial b. pt., °F.	92
Recovered, by volume	
5%	114
20%	149
50%	215
70%	266
90%	348
End point	410
Residue, % by vol.	1.0
Aromatics, % by vol.	24
Olefins, % by vol.	15
Saturates, % by vol.	61
Sulfur, Wt. %	0.141
Tetraethyl lead, g./gal	3.27*

*includes 0.5 mole ethylene dibromide and 1.0 mole ethylene dichloride per mole of tetraethyl lead.

The test procedure used was as follows:

Intake Valve Deposit Test

The engine used was a 1968, 250 cubic inch, 6 cylinder Chevrolet engine equipped with "Power-Glide" transmission and inertia flywheel.

TABLE I

CARBURETOR DETERGENCY TESTS
% CARBURETOR CLEAN-UP

		Polyoxyalkylene Compound						
			A			B	C	D
Polymer	Conc.(wt.%)	0	0.004	0.008	0.016	0.008	0.008	0.006
1. None	—	16	—	7	25	34	33	20
Polyisobutylene								
2. M.W. = 440	0.037	13	—	33	—	—	—	—
3. M.W. = 800	0.01	13	—	23	—	—	—	—
4. M.W. = 800	0.037	21	20	36	40	32	33	13
5. M.W. = 800	0.062	33	—	34	—	—	—	—
6. M.W. = 800	0.124	13	—	13	—	—	—	—
7. M.W. = 950	0.037	33	—	20	—	—	—	—
8. M.W. = 1400	0.031	13	—	19 (1)	—	—	—	—
Polypropylene								
9. M.W. = 840	0.037	20	—	20	—	13	—	20

(1)Average of two tests.

TABLE II

CARBURETOR DETERGENCY TESTS
% CARBURETOR CLEAN-UP INCREASE

		Polyoxyalkylene Compound						
				A		B	C	D
Polymer	Conc.(wt.%)	0	0.004	0.008	0.016	0.008	0.008	0.006
1. None	—	0	—	0	9	18	17	4
Polyisobutylene								
2. M.W. = 440	0.037	0	—	17	—	—	—	—
3. M.W. = 800	0.01	0	—	7	—	—	—	—
4. M.W. = 800	0.037	5	4	20	24	16	7	0
5. M.W. = 800	0.062	17	—	18	—	—	—	—
6. M.W. = 800	0.124	0	—	0	—	—	—	—
7. M.W. = 950	0.037	17	—	4	—	—	—	—
8. M.W. = 1400	0.031	0	—	5 [1]	—	—	—	—
Polypropylene								
9. M.W. = 840	0.037	4	—	4	—	0	—	4

[1]Average of two tests.

The engine was on a test stand equipped with a dynamometer to absorb the power output. The heads were completely reconditioned, deposits removed from piston tops and the carburetor overhauled. New PCV valve, spark plugs, points and gasoline filter were installed. The oil filter was changed and 10W–30 oil put in.

The test was performed by operating the engine for 80 1-hour cycles. Each cycle consisted of the following conditions designed to simulate stop-and-go on-the-road conditions including moderate and high speed driving alternating with stopped periods with the engine running such as at a traffic light.

Time Interval (mins.)	Engine Speed, rpm	Dyno Speed, rpm	Throttle
0–5	—	1300 50	Idle-WOT*
5–8	600	—	Idle
8–12	—	1700 50	Idle-WOT*
12–15	600	—	Idle
15–18	—	2050 75	Idle-WOT*
18–21	600	—	
21–26	—	1300 50	Idle
26–29	600	—	Idle-WOT*
29–34	—	2800 75	Idle
34–60	600	—	Idle-WOT*

*5 sec. idle, 5 sec. wide open throttle

The engine coolant fluid inlet and outlet temperatures, the engine oil temperature and pressure, the transmission oil temperature and the engine and dynamometer speeds were continuously recorded. The oil and spark plugs were changed at 40 hours.

At the end of the 80 cycles, the intake valves were removed, washed with pentane, dried and weighed. These valves were then cleaned by scraping off the tulip deposit and weighed again. The polyoxyalkylene compounds A and C are described in Example 2. The results are summarized in Table III.

TABLE III

		Intake Valve Deposit			
Polymer	M.W.	Conc. (Wt.%)	Polyoxyalkylene Compound	Conc. Lbs./1000 Bl.	Intake Valve Deposit (g.)
1. None	—	—	None	—	1.07(5)[1]
2. polyisobutylene	800	0.037	A	20	0.44(2)
3. polyisobutylene	1400	0.031	A	20	0.94(3)
4. polyisobutylene	1400	0.027	C	20	1.30(2)

[1]= number of runs.

These results show that the polyisobutylene and the polyoxyalkylene compound combination of the invention is particularly effective in reducing the intake valve deposit formation. It is also shown that when the polyisobutylene chosen is of higher molecular weight (e.g. 1400), the beneficial effects are not as pronounced.

EXAMPLE 4

This example illustrates the compatibility of the combinations of the present invention. Compatibility is defined in terms of weight percent of xylene required to form homogeneous solution when hydrocarbon polymer and polyoxyalkylene compounds are combined at 25°C.

The compatibility test is carried out by mixing 80 parts by weight of the hydrocarbon polymer and 20 parts by weight of the polyoxyalkylene compound at 25° to 30°C. If a clear solution is not obtained, xylene is added in increments with stirring until a clear solution results. The compatibility results are expressed in terms of weight per cent of xylene required to obtain a clear solution, the degree of compatibility decreasing with the increasing amount of xylene required. The results are summarized in the following table. The polyoxyalkylene compounds A and C are as described in Example 2.

Compatibility

Combination (80% polymer, 20% polyoxyalkylene Compound)

	Compatibility (Required % Xylene)
1. polyisobutylene (M.W.=440) + A	0
2. polyisobutylene (M.W.=800) + A	0
3. polyisobutylene (M.W.=950) + A	0
4. polypropylene (M.W.=840) + A	0
5. polyisobutylene (M.W.=1260)+ A	5
6. polyisobutylene (M.W.=1400)+ A	10
7. polyisobutylene (M.W.=800) + C	25
8. polyisobutylene (M.W.=1260)+ C	35
9. polyisobutylene (M.W.=1400)+ C	40

These results show that the preferred combination of polypropylene and polyisobutylene of the molecular weight in the range of from about 400 to 900 and of polyoxyalkylene compound,

$$R_{12-16}(OCH_2\underset{\displaystyle CH_3}{\underset{|}{CH}})_7OH,$$

formed homogeneous mixtures without the addition of any xylene solvent. As mentioned earlier, it is advantageous to have a combination which is homogeneous since the possibility of the components separating upon storage is eliminated and the cost of storage and transportation of the combination is minimized since only the active combination need to be stored and shipped.

As mentioned previously, the effectiveness of the additive combination as intake valve deposit modifier appears to be related to the degree of compatibility of the hydrocarbon polymer and the polyoxyalkylene compound. Thus as shown in this example, test 2 when 80 parts of polyisobutylene of 800 molecular weight is combined with 20 parts of

$$R_{12-16}(OCH_2\underset{\displaystyle CH_3}{\underset{|}{CH}})_7OH$$

where R_{12-16} is as defined previously, at 25°–30°C. a completely compatible (no xylene required) system is obtained and as shown in Example 3, test 2, this combination is effective in reducing the intake valve deposit formation. However, when 80 parts of polyisobutylene of 1,400 molecular weight is combined with 20 parts of the same

$$R_{12-16}(OCH_2\underset{\displaystyle CH_3}{\underset{|}{CH}})_7OH$$

at 25°–30°C., 10 weight percent of xylene is required to form a clear solution, this example, test 6, and as shown in Example 3, test 3, this combination is not as effective in reducing the intake valve deposit formation. Thus, a combination which is preferred as an intake valve deposit modifier is readily selected by carrying out the compatibility test as described.

EXAMPLE 5

The example illustrates the anti-icing properties of the combination of the invention. The anti-icing properties are determined by adding the additives to gasoline at different concentrations and then using the gasoline in a Engine Carburetor Anti-icing Test as described below. The test is carried out by using a Chevrolet 230 cubic inch, 6 cylinder engine. The environment of the carburetor is maintained at 40°F. and 95 percent relative humidity. Cool, essentially water-saturated air is thus drawn through the carburetor. The test consists of running the engine on a two-part cycle (1) 20 seconds with open throttle at 1600 rpm and (2) 10 seconds with the throttle almost closed at 400 rpm. During the test, ice forms on the throttle plate and causes the engine to stall by blocking the flow of air when the throttle plate is almost closed during the idle portion (400 rpm) of the test. Normally, in the absence of effective additives, the engine stalling occurs after about 3–4 cycles. Generally an additive is considered to be acceptable as anti-icing agent if it prevents stalling to about 10 cycles while a good anti-icing agent prevents stalling to about 25 cycles or more. A useful method of comparing relative effectiveness of several additives, as anti-icing agents, is to compare the amount of the particular additive required to obtain greater than 25 cycles to stall. The results summarized in the following table show that the additive combinations of the present invention are very effective as anti-icing agents. In each of the tests below, polyisobutylene of molecular weight of 440 and 800 was present in the amount of 0.031 weight per cent of the gasoline.

Anti-icing Tests

Polyisobutylene	$R(OCH_2\underset{\displaystyle CH_3}{\underset{|}{CH}})_xOH$	Concentration of $R(OCH_2\underset{\displaystyle CH_3}{\underset{|}{CH}})_xOH$ to Give 25 Cycles (lbs./1000 bbles)
1. M.W. = 440	$R=C_{12}-C_{16}$, $x=6$	> 50
2. M.W. = 440	$R=C_{12}-C_{16}$, $x=7$	20
3. M.W. = 440	$R=C_{12}-C_{16}$, $x=9$	20
4. M.W. = 800	$R=C_{12}-C_{16}$, $x=6$	> 50
5. M.W. = 800	$R=C_{12}-C_{16}$, $x=7$	20
6. M.W. = 800	$R=C_{12}-C_{16}$, $x=9$	20

EXAMPLE 6

This example illustrates that the additive combinations of the invention are useful when used with anti-rust additives. Dimer acids, such as dimers of linoleic acid, are known in the art as rust inhibitors for petroleum products (e.g., U.S. Pat. Nos. 2,631,979 and 2,632,695). An additive formulation comprising (by weight) (a) polyisobutylene (M.W. 800), 62.0 percent; (b) "Santolene" C (dimer acid sold by Monsanto), 3.3 percent; (c) above described preferred polyoxyalkylene compound

$$(R(OCH_2\underset{\displaystyle CH_3}{\underset{|}{CH}})_xOH$$

wherein R is a mixture of alkyl groups of 12 to 16 carbon atoms and x has an average value of 7, 13.3 percent, and (d) xylene, 21.4 percent was added to gasoline at a concentration of 150 pounds per thousand barrels. The performance tests carried out as described in the previous examples showed carburetor clean-up of

36 percent, intake valve deposit of 0.51 gram and icing test cycles of greater than 25. In addition, the gasoline blended with the above additive composition showed rust rating of "pass" by ASTM D-665 Method and Federal Water rating of 1 as determined by Federal Test Method Standard No. 3251.7 whereby the gasoline mixture is shaken with a phosphate buffer and the condition of the interface noted. A rating of 1 designates clear and clean interface.

EXAMPLE 7

This example illustrates that the additive compositions of the invention are useful when used together with anti-stall additives in gasoline. In U.S. Pat. No. 3,336,123 a gasoline anti-stall composition is disclosed which composition is a salt of (a) linoleic acid dimer and trimer and (b) a dialkylamino propyl carboxamide such as N(3-dimethylaminopropyl) oleamide. An additive formulation was prepared by mixing (by weight) (a) polyisobutylene (M.W. 730), 52.0; (b) "Santolene" C (dimer acid sold by Monsanto), 3.3 percent; (c) above described preferred polyoxyalkylene compound

$$R(OCH_2\underset{\displaystyle CH_3}{\underset{|}{CH}})_xOH$$

wherein R is a mixture of alkyl groups of 12 to 16 carbon atoms and x has an average value of 7, 13.3 percent; and (d) xylene, 21.4 percent (e) N(3-dimethylaminopropyl) oleamide, 10.0 percent. This additive composition was added to gasoline at a concentration of 150 pounds per thousand barrels. The performance tests carried out as described previously showed carburetor clean-up of 35 percent; intake valve deposit of 0.69 gram; icing test cycles of greater than 25; rust rating of "pass;" and Federal Water rating of 1.

The embodiments of the invention in which an exclusive property, or privilege is claimed are defined as follows:

1. Multi-functional fuel additive compositions suitable for use in hydrocarbon fuels to impart anti-icing and carburetor detergency consisting essentially of

A. Polyisobutylene having a molecular weight of from about 400 to about 900, and

B. from about 10 to 160 percent by weight of said polyisobutylene of a polyoxyalkylene compound of the formula

$$R(OCH_2\underset{\displaystyle CH_3}{\underset{|}{CH}})_xOH$$

wherein R is alkyl of 10 to 18 carbon atoms, and x has an average value of 4 to 20.

2. A composition of claim **1** wherein the polyoxyalkylene compound is one of the formula

$$R(OCH_2\underset{\displaystyle CH_3}{\underset{|}{CH}})_xOH$$

wherein x has an average value of from 5 to 10.

3. A composition of claim **1** wherein the value of x in the polyoxyalkylene compound is about 7, and R is a mixture of alkyl group of 12 to 16 carbon atoms.

4. A liquid hydrocarbon fuel composition characterized by improved anti-icing and carburetor detergency comprising

A. a major portion of a liquid hydrocarbon fuel comprising hydrocarbons boiling in the gasoline range, and based on the weight of said fuel

B. about from 0.01 to about 0.06 percent by weight of polyisobutylene having a molecular weight of from about 400 to about 900 and

C. from about 0.008 to about 0.016 percent by weight of a polyoxyalkylene compound of the formula

$$R(OCH_2\underset{\displaystyle CH_3}{\underset{|}{CH}})_xOH$$

wherein R is an alkyl group of 10 to 18 carbon atoms, and x has an average value of 4 to 20.

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