

March 7, 1967

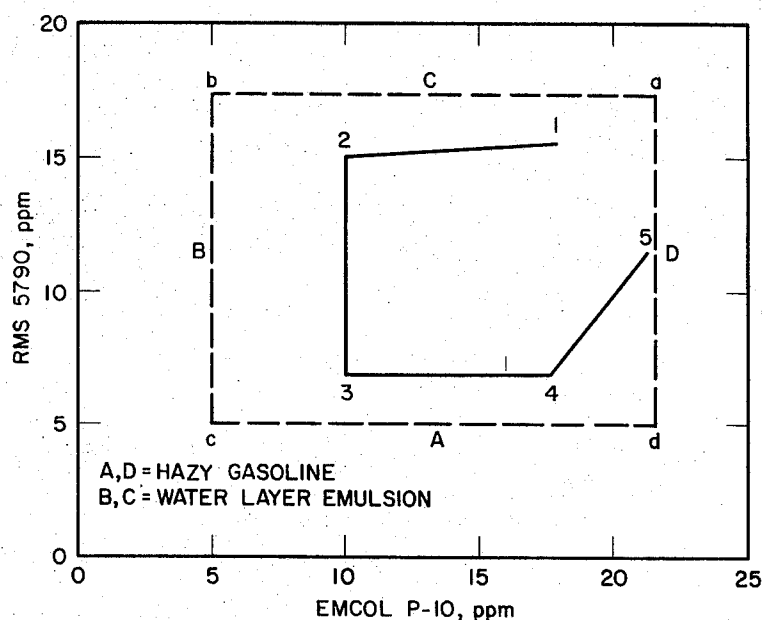
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3,307,928

GASOLINE ADDITIVES FOR ENHANCING ENGINE CLEANLINESS

Filed Jan. 30, 1963

A RANGE OF EFFECTIVE EMCOL P-10/RMS 5790
CONCENTRATIONS (AND RATIOS) DEFINED
FOR DETERGENT CONTAINING FUEL



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3,307,928

GASOLINE ADDITIVES FOR ENHANCING ENGINE CLEANLINESS

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Filed Jan. 30, 1963, Ser. No. 254,878

7 Claims. (Cl. 44-63)

This invention relates to an improved motor fuel composition, and particularly to internal combustion engine fuels containing multifunctional additives which are especially useful in enhancing overall engine cleanliness.

Despite the high efficiency of modern gasoline engines, complete combustion of fuel introduced into the combustion chambers of such engines seldom, if ever, occurs. Studies have shown that certain polynuclear aromatic compounds and other relatively high boiling materials present in gasolines are only partially burned and that the exhaust and blow-by gases formed in the combustion chambers of gasoline engines contain trace amounts of hydrocarbons. Apparently these hydrocarbons undergo complex cracking, polymerization and oxidation reactions to form sludge and varnish precursors which enter the crankcase past the piston rings. Deposits, sludge and varnish formed in this manner seriously affect the operation of a gasoline engine. These deposits promote wear, valve lifter sticking and generally poor engine performance and indirectly contribute to surface ignition, spark plug fouling, octane requirement increase, and other combustion difficulties.

In the past, various detergent and dispersant type additives have been employed in the nonvolatile, high boiling crankcase mineral lubricating oil to effect engine cleanliness. This procedure has been effective to a degree. However, in those cases where the oil is left in the engine over relatively long periods, the detergent additives are depleted. This, of course, results in a reduction in the cleaning effectiveness of the lubricating oil.

It is, therefore, an object of this invention to provide a method of maintaining engine cleanliness irrespective of the depletion of the detergents ordinarily employed in lubricating oil.

It is another object of this invention to provide superior detergent additives for enhancing overall engine cleanliness.

It is a further object of this invention to provide an additive package which does not cause a water haze to form in the gasoline.

The objects of this invention are obtained in part by employing a combination of detergent additives in gasoline which survive combustion and are continuously added to the engine crankcase oil. It has been found that adding the detergent in this manner enhances overall engine cleanliness, not merely the cleanliness of those engine parts contacted with the gasoline. The detergent additives seep past the rings into the lubricating oil, and also may inhibit sludge precursors in the gasoline so as to prevent deposit formation. The effect is that of maintaining continuous detergent action in the engine.

There are other substantial advantages to be obtained from employing the detergent additives in gasoline. The additives of this invention, in addition to reducing crankcase sludge and the like, reduce intake system deposits, prevent corrosion, and improve gasoline storage stability.

The improved detergent action is obtained by employing a combination of additives. This combination substantially reduces crankcase sludge. However, when added to gasoline, the combination causes a haze to be formed if the gasoline comes into contact with small quantities of water. Such contacting is almost inevitable. In many

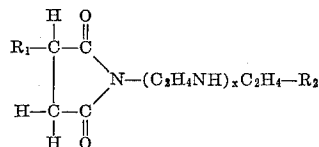
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instances, the haze has no serious effect on the use of the gasoline. However, in cold weather there exists the problems of carburetor icing and fuel line freezing. Therefore, such a haze is undesirable. Elimination of this haze caused by the combination of detergents presented a difficult problem. Many additives and combinations of dehazing additives were tried and found to be ineffective in eliminating the haze caused by the detergent additives of this invention. A combination of additives was discovered which is quite effective in reducing and in many cases virtually eliminating the haze. The additives of the combination must be employed in certain critical proportions as described hereinafter.

The combination of detergent additives is best employed in conjunction with a high boiling oil.

The two detergent additives and the high boiling oil have utility when employed individually, but enhanced results, with regard to reduction of crankcase sludge, are obtained by employing the additives in combination.

In this invention, three additives are employed in order to enhance engine cleanliness. The first is a polyolefin succinimide having the following formula:

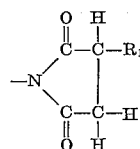


wherein R_1 is a polyolefin such as polyisobutylene, polypropylene and the like. The polymer should have a molecular weight of from 780 to 1500. It can be substituted or unsubstituted, but, preferably is unsubstituted.

x is in the range of from 1 to 3 inclusive.

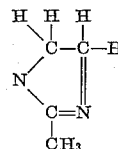
R_2 is selected from the group consisting of

(1)



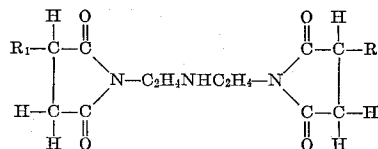
and

(2)



ADDITIVE A

The preferred polyolefin succinimide has the following formula:



wherein R_1 is polyisobutylene having a molecular weight of from 780 to 1500. The succinimide having the above formula is hereinafter referred to as Additive A.

The polyisobutylene succinimide can be prepared by azeotropically distilling polyisobutylene succinic anhydride, prepared from 900 mol wt. polyisobutylene, with an amine. The distillation is performed until no additional water is formed.

The second additive utilized in this invention is a phosphosulfurized hydrocarbon, and preferably a phosphosulfurized polyolefin. The phosphosulfurization agent

may be P_2S_3 , P_2S_5 , P_4S_3 , P_4S_7 , or their mixtures, or mixtures of elemental phosphorus and sulfur or other materials. A sulfide of phosphorus, especially phosphorus pentasulfide (P_2S_5) is preferred. Generally, in the range of about 1.0 to 50.0% by weight, based on the hydrocarbon, of phosphosulfurizing agent is used. A preferred range is about 5 to 25, e.g. 10 to 20, wt. percent.

Hydrocarbons to be treated should, of course, be reactive with the phosphosulfurizing agent. They include olefins, diolefins, acetylenes, aromatics, cyclic aliphatics, and various mixtures of these such as are found in petroleum fractions, condensation products of petroleum fractions, hydrogenated coals, synthetically produced hydrocarbons and the like. Preferred are lubricating oil distillates and base stocks such as bright stock residue and the like and polyolefins.

The phosphosulfurized hydrocarbons which are utilized as one constituent of the additive combination of the invention are prepared by reacting a C_2 to C_6 olefin polymer with a sulfide of phosphorus. Olefinic polymers prepared by the polymerization or copolymerization of low molecular weight olefins and diolefins such as ethylene, propylene, butylene, isobutylene, butadiene, isoprene, and cyclopentadiene, are suitable materials for the phosphosulfurization. Polymers of monoolefins wherein the molecular weight ranges from about 500 to about 20,000 and preferably ranges from about 600 to about 10,000, e.g. 700 to 2,000 are particularly effective in preparing the phosphosulfurized hydrocarbons of the invention. The most preferred polyolefin employed is a polyisobutylene or polybutene having an average molecular weight of 700 to 1,200, e.g. 940.

One method of carrying out such a polymerization reaction is to employ a Friedel-Crafts catalyst such as boron fluoride or aluminum trichloride at low temperatures in the range of from about 0° F. to about -40° F. Other methods familiar to those skilled in the art, carried out at higher temperatures and with other polymerization catalysts may also be used as described, for example, in U.S. Patent 2,768,999.

The resulting acidic phosphosulfurized hydrocarbon reaction product is then hydrolyzed by steam stripping the product at a temperature of between 100° C. and 200° C., e.g. 140° C. to 160° C., for a period of time, e.g. 1 to 6 hours, sufficient to reduce the volatile by-product odor and to bring the acid number to at least 25 and the sulfur content to less than 1.5 wt. percent. This method is more fully described in British Patent 838,928.

The hydrolyzed phosphosulfurized polyolefin is then preferably treated with ethylene oxide or urea. Moreover, the hydrolyzed phosphosulfurized polyolefin is further stabilized and improved by reacting the acidic hydrolyzed product with a neutralizing agent such that its titratable acidity is at least partially reduced. Neutralizing agents include the alkali and alkaline earth and metal hydroxides, carbonates and oxides, but preferably include those ashless basic reagents such as ammonia and alkyl and aryl substituted amines and polyamines as previously described. The amount of neutralizing agent employed is usually between 1 to 50% by weight of the acidic product, e.g., 1 to 20 wt. percent, or from 1 to about 10 moles, e.g., 2 to 5 moles, of agent to moles of acidic product, e.g., 2 to 6 moles.

A most preferred class of basic reagents includes organic epoxide compounds such as aryl substituted alkyl epoxides like styrene epoxide; alicyclic epoxides like cyclopentene epoxide; halosubstituted alkylene epoxides such as chloropropylene oxide; and particularly C_1 to C_6 alkylene oxides such as ethylene oxide, propylene oxide, butene oxide, and the like. From 1 to 10 moles of these epoxides are reacted with each mole of acidic product as described more fully in British Patent 792,553, hereby incorporated by reference. Although the neutralized product is preferred and the hydrolyzed and neutralized product most preferred, the untreated P_2S_5 polyolefin reaction product

itself may be employed, but generally would somewhat reduce the effectiveness.

The preferred phosphosulfurized polyolefin is prepared as follows:

ADDITIVE B

Polybutene having a molecular weight of from 700 to 1200, e.g., 940, is reacted with P_2S_5 as described above. The phosphosulfurized polybutene is then hydrolyzed by steam stripping at a temperature of about 150° C. for a time sufficient to bring the acid number to at least 25. The product is then ethoxylated by reacting it with from 1 to 6 moles of ethylene oxide per mole of acidic product. This additive is hereinafter referred to as Additive B.

The third additive of this invention is a high boiling solvent oil of petroleum derivation. The oil should have a boiling range of within 350° F. to 800° F. at 10 mm. of Hg and preferably between 400° F. and 700° F. The oil should have a viscosity within the range of from 45 SSU/210° F. to 150 SSU/210° F. Typical inspection for an oil of this type is as follows:

ADDITIVE C

Gravity, ° API	28.8
Sulfur, wt. percent	0.40
Neutralization No. D974	0.02
Aniline Point, ° F.	273.5
ASTM distillation, 10 mm. Hg vacuum:	
IBP, ° F.	353
10% Point, ° F.	464
50% Point, ° F.	534
90% Point, ° F.	626
F.B.P. ° F.	694
Conradson carbon residue	0.1
Vis/210° F., SSU	60.7

The oil, Additive C, is the one which was employed in tests hereinafter described.

The motor fuels in which the additives are employed in order to enhance engine cleanliness are conventional petroleum distillate fuels boiling in the gasoline boiling point range employed in internal combustion, preferably spark ignition, engines. They are supplied in a number of different grades depending upon the type of service for which they are intended. The additives may be employed in all of these grades but are particularly useful in motor and aviation gasolines. Motor gasolines as referred to in connection with the present invention are defined by ASTM Specification D-439-58T in Types A, B and C. They are composed of a mixture of various types of hydrocarbons including aromatics, olefins, paraffins, isoparaffins, naphthenes and, occasionally, diolefins. Those motor fuels containing at least 10% by volume of thermally or catalytically cracked high aromatic components may be especially benefitted from the instant invention. Suitable gasolines to which the polymeric additives of the instant invention may be added are those gasolines having an octane number range of 83 to 105 or higher, such as a clear octane number of over 90, for example, over 95 or 100, and comprising over 20% by volume of aromatic hydrocarbons and less than 30% by volume of olefinic hydrocarbons. They are derived from petroleum crude oil by refining processes such as fractional distillation, catalytic cracking, hydroforming, alkylation, isomerization, polymerization and solvent extraction. Motor gasolines normally have boiling ranges between about 70° F. and about 450° F., while aviation gasolines have narrower boiling ranges of between 100° F. and 330° F. The vapor pressures of gasoline as determined by ASTM Method D-86 vary between about 7 and about 15 p.s.i. at 100° F. The copolymers may also be employed in aviation gasolines which have properties similar to those of motor gasolines, but normally have somewhat higher octane numbers and narrower boiling ranges. The properties of aviation gasolines are set forth in U.S. Military

Specification MIL-F-5572 and ASTM Specification D-910-57T.

The copolymeric additives employed in accordance with the invention may be used in gasolines with other additive agents conventionally used in such fuels. It is common practice to employ from about 0.5 to about 7.0 cc./gal. of alkyl lead antiknock agents, such as tetraethyl lead, tetramethyl lead, dimethyl diethyl lead or a similar alkyl lead antiknock agent or olefinic lead antiknock agents such as tetraviny lead, triethyl vinyl lead, and the like, or a combination thereof, in both motor gasolines and in aviation gasolines, e.g., 1.0 to 3.0 cc. of tetraethyl lead-tetramethyl lead combination. Antiknock agents may also include other organometallic additives containing lead, iron, nickel, lithium, manganese and the like. Other additives such as those conventionally employed in gasolines may be used such as corrosion inhibitors, anti-oxidants, antistatic agents, lead octane appreciators like t-butyl acetate, auxiliary scavengers like tri-B-chloroethyl phosphate, dyes, anti-icing agents like isopropanol, hexylene glycol and the like.

Catalytically and thermally cracked and reformed gasolines containing a high aromatic content, whether leaded or unleaded, are particularly prone to yield excessive crankcase sludge and induction system deposits and are improved by addition of the applicants' polymeric additives.

Enhanced engine cleanliness is obtained by employing the polyolefin succinimide and the phosphosulfurized polyolefin in combination in gasoline.

The additives are employed in a range of ratios from 1:3 to 3:1 parts by volume of the polyolefin succinimide to the phosphosulfurized polyolefin, the preferred range of ratios being from 1:1 to 3:1 parts by volume of the polyolefin succinimide to the phosphosulfurized polyolefin. The preferred ratio being 2/1. The additive combination comprising the polyolefin succinimide and the phosphosulfurized polyolefin is employed in gasoline in a minor amount sufficient to enhance engine cleanliness. The combination is advantageously utilized in concentrations ranging from 0.1 to .001 vol. percent, and preferably from .03 to .01 vol. percent.

The high boiling oil assists the additive combination through the combustion zone into the crankcase of an engine. The oil is utilized in concentrations of from 0.005 to 0.5 vol. percent, and preferably from 0.005 to 0.25 vol. percent.

The efficacy of the additive combination is demonstrated by the following example.

Example 1

Ford 4-45 sludging tests were performed in order to determine the sludge inhibiting effect of the additive combination. The additive combination consisting of 2 parts by volume of Additive A to 1 part by volume of Additive B was added in a concentration of 0.02 vol. percent to a gasoline having the following specifications:

ASTM distillation:	
10% B.P., ° F.	131
50% B.P., ° F.	215
90% B.P., ° F.	330
F.B.P., ° F.	425
Gravity, °API	59.3
Reid vapor pressure	9.6
ASTM Gum	2.2
TEL, cc./gal.	2.1

The gasoline composition was then employed in a 6-cylinder Ford engine, and said engine was operated for 55 hours, then inspected, and test was continued to 110 hours. The following engine parts were examined:

Rocker Arm Cover	P.R.C. Cover
Rocker Arm Assembly	Crankcase (oil pan)
Cylinderhead	Crankshaft

Push Rod Chamber

Timing Gear Cover
(@ 110 hours only)

An over-all merit rating of from -3 to 10 was then assigned the engine based upon the inspection. On the merit rating scale, 10 is perfect, i.e. no sludge, whereas 0 connotes extremely heavy sludge.

The same test was performed with the gasoline not containing the additive combination and with the gasoline containing only Additive A in a concentration of .02 vol. percent.

Results of these tests appear in Table I.

TABLE I.—FORD 4-45 TESTS

	Run		
	1 Base*	2 Base plus .021 Vol. Percent Additive A	3 Base plus .014 Vol. Percent Additive A and .007 Additive B
Sludge:			
55 hours....	7.9	9.1	9.5
110 hours..	6.4	7.4	7.9

*Average of four base tests.

The data show that Additive A is effective in enhancing engine cleanliness. The merit ratings, 9.1 and 7.4 (110 hours), obtained by using .021 vol. percent of Additive A were substantially better than the merit ratings, 7.9 and 6.4, obtained by using only the base gasoline.

The results obtained in Run 3 were better than those obtained in either Runs 1 or 2. In Run 3, the total amount of additive combination was the same as the quantity of Additive A employed in Run 2. Even though improvement is difficult to obtain above a merit rating of 9, the additive combination, Run 3, proved to be superior to Additive A.

Example 2

Sludge tests were performed as in Example 1 to determine the effect of adding a high boiling oil to the gasoline containing the combination of detergent additives. The oil was added in a concentration of 0.1 vol. percent to the gasoline described in Example 1. The gasoline also contained the additive combination described in Example 1. The results of the Ford 4-45 Sludging Tests appear in Table II.

TABLE II.—FORD 4-45 SLUDGING TEST

	Base plus .014 Vol. Percent Additive A plus .007 Vol. Percent Additive B plus 0.1 Vol. Percent H.B.O., Additive C
Sludge:	
55 hours....	9.6
110 hours....	8.8

The oil proved to be effective in enhancing the effect of the additive combination. It is seen that the merit ratings obtained are better than those of the additive combination as depicted in Table I. There was almost a one merit improvement in performance as is seen in comparing the data in Run 3 of Table I with the above data.

Infrared studies show that more of the detergent additive survives combustion and passes into the crankcase when a high boiling oil is used in conjunction with said detergent additives. It is believed that the oil protects the less stable detergent additives. This oil also enhances performance of other detergents added to gasoline.

The above examples clearly demonstrate the enhanced cleanliness obtained by the use of a combination of a polyolefin succinimide and a phosphosulfurized polyolefin. The examples also show that the efficacy of

the combination can be improved, particularly over long periods of operation, by utilizing a high boiling oil in conjunction with said combination.

The additives described are effective in enhancing engine cleanliness. However, the addition of these additives to gasoline creates a problem of haze formation. Under most operating conditions, the water haze will not seriously affect the operation of internal combustion engines. However, in cold weather, the haze promotes carburetor icing and fuel line freezing and is, thus, undesirable.

At first blush, it might appear that the problem could be easily solved by employing any known dehazer or demulsifier. However, many such materials were tried, individually and in combination, and found to be ineffective.

It has now been discovered that a particular combination of additives employed in critical proportions greatly reduce and in many instances virtually eliminate the haze problem.

ADDITIVE D

Dodecylbenzene sulfonic acid is one of the additives of the combination employed to effect a separation of gasoline and water. This additive can be prepared by reacting dodecylbenzene with concentrated sulfuric acid. This material is readily available on the market. For example, EMCOL P-10 hereafter referred to as additive D is dodecylbenzene sulfonic acid.

ADDITIVE E

The second additive is an ethoxylated fatty acid polyester. This additive can be prepared by reacting a dimeric fatty acid, e.g., dimeric oleic acid, with trimethylol propane. The resulting polyester product is then reacted with ethylene oxide in a ratio of 2 parts by weight of the polyester per part of ethylene oxide. For example, RMS 5790 is the ethoxylated fatty acid polyester employed in the following tests and is hereafter referred to as Additive E.

The dehazing additive combination is effective in concentrations of from 10 p.p.m. to 40 p.p.m., and preferably from 17 p.p.m. to 35 p.p.m. The weight ratio of dodecylbenzene sulfonic acid to ethoxylated fatty acid polyester is from 0.3 to 4.5, and preferably from 0.67 to 2.4.

Haze formation presents two problems to be solved. First, a suitable additive must eliminate the water haze in the gasoline. Second, it must separate the gasoline from the water phase which may accumulate in storage tanks and the like. In short, an additive must effect a complete separation of gasoline and water.

The efficacy of the instant additive combination is demonstrated by the following example:

Example 3

Haze tests were performed in order to determine the efficacy of the dehazing additive combination. A gasoline having the following specifications was employed in the tests:

ASTM Distillation:

I.B.P.	90
10% B.P.	106
50% B.P.	196
90% B.P.	302
F.B.P.	360
Gravity, ° API	59
Reid vapor pressure	11.0
Sulfur, wt. percent	0.20
Research octane number	98
Motor octane number	88
Tetraethyl lead, cc./gal.	2.5

Additive A and Additive B in a weight ratio of 2:1 were added to the gasoline. Additive C was added in a concentration of 0.1 vol. percent.

Service station water bottoms were added to 450 ml. of the gasoline composition in a concentration of 1 vol. percent. The fuel was then placed in a Waring Blendor for 1 minute at 3500 r.p.m. After 6 hours, the fuel was still very hazy.

Additive D and Additive E in a weight ratio of 3:2 were added to the gasoline containing Additives A, B and C. To 450 ml. of this fuel composition was added 1 vol. percent of service station water bottoms. The composition was then stirred in a Waring Blendor for 1 minute at 3500 r.p.m. Tests were run with various concentrations of additives. The results appear in Table III. The gasoline composition was examined 6 hours after stirring and given a haze rating. A rating of 1 corresponds to a completely clear composition whereas a composition with a rating of 8 was very hazy.

TABLE III

	Additive A plus Additive B, Vol. Percent	Additive C, Vol. Percent	Additive D plus Addi- tive E, p.p.m.	Haze Results (6 hrs. after stirring)	
				Gasoline Phase	Water Phase
20	0.030.....	0.1	36	1	Clear.
25	0.021.....	0.1	25	1	Do.
	0.015.....	0.1	18	1	Do.
	0.0075.....	0.1	9	1	Do.

These data show that the instant dehazing additive combination is effective in eliminating haze caused by the detergent additives throughout a rather broad range of concentrations. The data show that the dehazing combination is effective at low concentrations that may result due to dilution occurring during handling of the fuel.

The additive combination not only provides a clear gasoline phase, but also a clear water phase. In short, the combination effects a complete separation of gasoline and water.

Example 4

The dehazing additive combination should be employed within a narrow range of ratios of Additive D to Additive E.

A 450 ml. sample of the gasoline composition was combined with 1 vol. percent water and stirred in a blender for 1 minute at 3500 r.p.m. The gasoline phase and the water phase were then examined for clarity. The base cleared within 6 hours.

The accompanying drawing depicts a phase diagram which shows the concentrations and proportions of the additive combination which are effective. The area delineated by FIGURE 1-2-3-4-5 is one in which the additive combination effected essentially a complete separation of gasoline and water. This separation is obtained by employing the additive combination in a concentration of from 17 to 35 p.p.m. and within a range of weight ratios of from about 0.67/1 to 2.4/1 parts of EMCOL P-10 to RMS 5790. FIGURE 1-2-3-4-5 was determined from data obtained as follows:

To the gasoline, described in Example 3, were added 0.1 vol. percent of Additive C and 0.021 vol. percent of the detergent combination consisting of 2 parts of Additive A to 1 part by volume of Additive B. To a number of 450 ml. samples of this gasoline concentration, the dehazing additive combination, Additive D and Additive E were added in various concentrations and proportions. FIGURE a-b-c-d delineates an area wherein a complete separation of gasoline is not effected, but where the results are better than the gasoline containing only Additives A, B and C. Outside of FIGURE a-b-c-d there results a gasoline in water emulsion, a water in gasoline emulsion, or both.

In summary, this invention provides a useful package of gasoline additives. It provides a combination of detergent additives which continuously enhance over-all engine cleanliness. Moreover, by employing certain high boil-

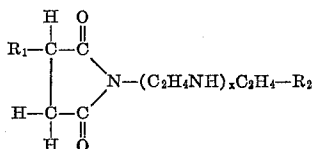
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ing oils with said combination, the detergent effect can be greatly enhanced, especially over long periods of operation. In addition, a combination of dehazing additives is provided which, when used in critical proportions, obviates the problem of haze formation encountered when detergents are added to gasoline.

What is claimed is:

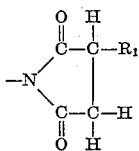
1. A motor fuel composition comprising a major proportion of a petroleum distillate fuel boiling in the gasoline range, a minor amount sufficient to enhance engine cleanliness, of an additive combination comprising:

(A) A polyolefin succinimide having the following formula:



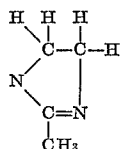
wherein R_1 is a polyolefin having a molecular weight of from 780 to 1500, x is in the range of from 1 to 3 inclusive, and R_2 is selected from the class consisting of:

(1)



and

(2)



and

(B) a phosphosulfurized polyolefin having a molecular weight of from 500 to about 20,000; wherein said additive combination is employed in the ratio of from 1:1 to 3:1 parts by volume of the polyolefin succinimide per part by volume of the phosphosulfurized polyolefin;

and a second additive combination in an amount sufficient to substantially separate said petroleum distillate fuel from water which it may contact, said additive combination comprising:

(C) dodecylbenzene sulfonic acid, and

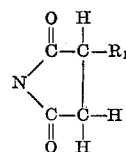
(D) an ethoxylated fatty acid polyester, said second additive combination being employed in a weight ratio of dodecylbenzene sulfonic acid to ethoxylated fatty acid ester in a range of from 0.3:1 to 4.5:1.

2. A motor fuel according to claim 1 wherein said first named additive combination constitutes from 0.001 to 0.1 volume percent of the motor fuel.

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3. A fuel according to claim 1 containing from 0.005 to 0.5 volume percent of a high boiling oil having a viscosity of from 45 SSU/210° F. to 150 SSU/210° F.

4. A motor fuel according to claim 1 wherein $x=1$, R_2 is



and R_1 is a polyolefin having a molecular weight of from 780 to 1500.

5. A motor fuel according to claim 1 containing a minor amount of a solvent oil of petroleum derivation having a boiling range within 350° to 800° F. at 10 mm. Hg.

6. A motor fuel according to claim 1 wherein said second additive combination is in a concentration of from 10 to 40 p.p.m.

7. A motor fuel according to claim 1 wherein said ratio is from 0.67:1 to 2.4:1 and said second additive combination is in a concentration of from 17 to 35 p.p.m.

References Cited by the Examiner

UNITED STATES PATENTS

2,296,069	9/1942	Talbert	44-76
2,316,739	4/1943	Cook et al.	44-76
2,334,239	11/1943	Barnett	252-56 X
2,371,333	3/1945	Johnston	252-51.5
2,568,876	9/1951	White et al.	252-51.5
2,700,022	1/1955	Clayton	252-56
2,995,428	8/1961	Godar	252-402 X
3,018,250	1/1962	Anderson	252-51.5 X
3,018,291	1/1962	Anderson	252-51.5 X
3,024,195	3/1962	Drummond	252-51.5
3,048,544	8/1962	Stewart	252-51.5
3,068,082	12/1952	Paris	44-63
3,080,223	3/1963	Monnikendam	44-62
3,131,150	4/1964	Stuart et al.	252-51.5
3,154,560	10/1964	Osuch	252-51.5
3,172,892	3/1965	Le Suer	252-51.5
3,216,936	11/1965	Le Suer	252-51.5
3,219,666	11/1965	Norman	252-51.5

FOREIGN PATENTS

792,553	7/1956	Great Britain.
838,928	10/1958	Great Britain.

OTHER REFERENCES

Esters by Glyco, published by Glyco Products Inc., Brooklyn 1, New York, January 1954.

Polyethylene Glycol Esters, publicized by Kessler Chemical Co., Inc., Philadelphia 35, Pa., received in U.S. Patent Office Dec. 20, 1948.

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