Aug. 30, 1960 M. R. BARUSCH ET AL 2,950,960

HYDROCARBON FUELS

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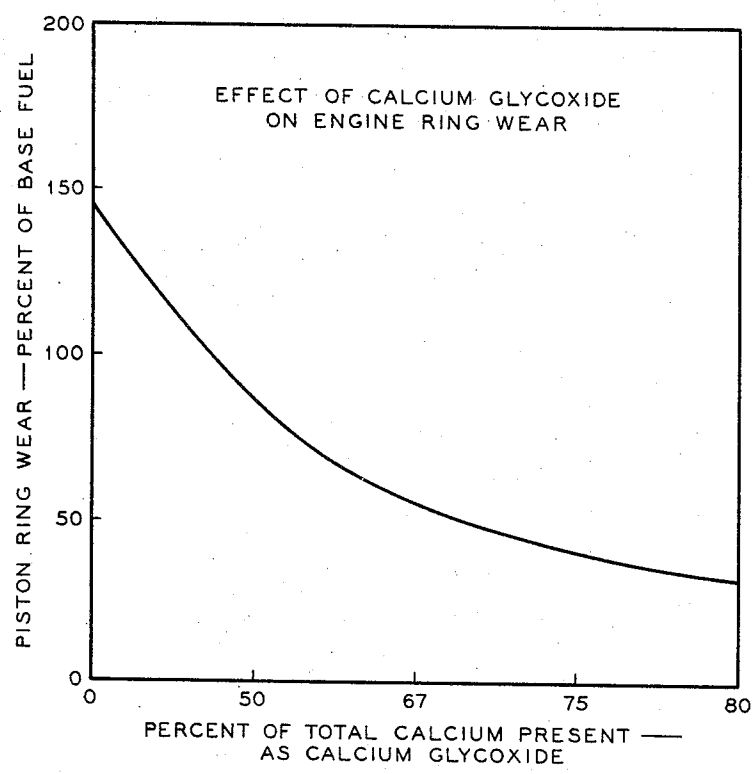


FIG. 1

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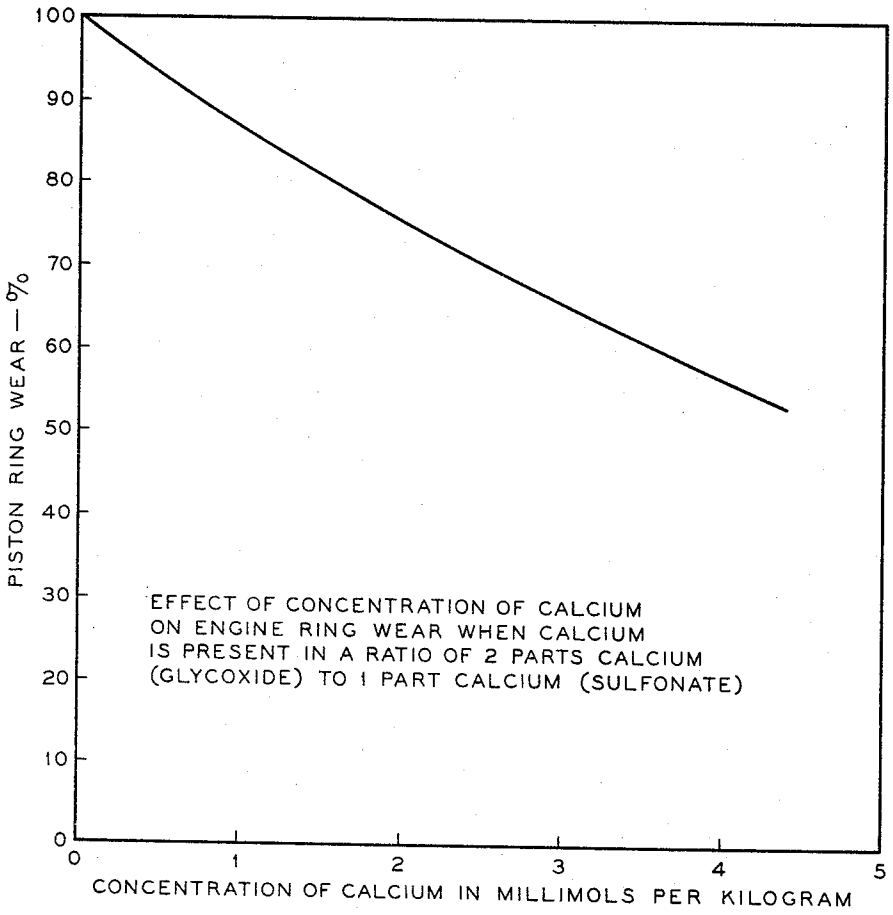


FIG. 2

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HYROCARBON FUELS

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10 Claims. (Cl. 44—63)

This invention relates to improved fuels for both spark- and compression-ignition engines, and more particularly, to fuels for such engines containing additives which substantially reduce engine wear incident to the combustion of the fuel.

It is an established fact that normal operation of spark- and compression-ignition engines with conventional fuel and lubricating oil compositions results in considerable wear of various parts of the engine. This wear greatly reduces engine efficiency and ultimately requires complete engine overhauling with replacement of pistons and piston rings, as well as reboring or replacement of the combustion chamber liners. Additionally, normal engine operation of compression-ignition engines with conventional fuels and lubricating oils results in substantial deposition of components of the fuel and combustion products thereof in injector tips and at other locations within the combustion chamber, including the exhaust valves. For example, such depositions in the injector tips alter the normal fuel spray pattern and result in highly inefficient engine operation due to incomplete combustion of the fuel.

A number of proposals have been made to reduce wear in order to eliminate engine overhauling and, in the case of compression-ignition engines, the reduction of deposition of the injector tips. Generally, these proposals include the employment of various metal alloys of low wearing characteristics in the combustion chambers, highly compounded lubricating oils, and various refinements of the fuel.

While these proposals have somewhat improved engine life through decrease in wear and engine deposition, they have long been recognized as falling short of their ultimate goal. Recently, the swelling demand for fuels and the lack of supply of many low sulfur crude oils has led to a tendency on the part of the petroleum industry to increase the sulfur content of the fuels. This factor has greatly aggravated an already undesirable condition. It is well recognized that engine wear rates, in both spark or combustion-ignition engines, are increased markedly as the sulfur content of the fuel increases. This wear increase, due to sulfur, is generally attributed to the corrosive acidic action of the products of combustion of the sulfur compounds on the internal surfaces of the combustion chamber.

Recently, it has been determined that the products of combustion of the hydrocarbon components of the fuel are corrosive to the metal surfaces of the combustion chamber. Furthermore, many fuel additives, for example, contain substantial amounts of naturally occurring sulfur compounds which, in themselves, represent still another source of corrosion activity. Also, in the case of gasoline containing tetraethyl lead, the halogen scavenging agents frequently employed therewith are known to form acidic compounds during combustion of the fuel, thereby leading to further corrosion.

In the light of the above-noted findings, it can be seen that one of the major causes of engine wear is the formation of various types of acids during operation which are extremely corrosive. Accordingly, it has been suggested that the neutralization of these acids offers a logical and effective means of reducing wear. For example, it has been suggested by Vinograd et al. (U.S. Patent No. 2,671,758) that colloidal dispersions of alkaline earth metal basic substances be added to lubricating oils and fuels.

Thus, in accordance with the present invention, it has been found that further improvements for the reduction of wear can be realized in the case of fuels for internal combustion engines by adding to the base fuel a minor proportion of a calcium or barium glycoxide and an oil-soluble metal sulfonate selected from the identical group of metals. Because of the higher basicity attained thereby, fuel compositions containing the metal glycoxide-metal sulfonate additive effectively neutralize higher amounts of acids than heretofore realized.

The base fuels of the compositions of this invention may be broadly described as those hydrocarbons suitable for use in all types of spark and compression-ignition type engines. Among these fuels are those hydrocarbons boiling within the gasoline range, that is, having an ASTM D–86 distillation within about 90° F. to about 425° F. Also included in the term "hydrocarbon fuel" are those base fuels composed of hydrocarbons boiling within the diesel boiling range, that is, having an ASTM D–158 distillation within about 325° F. to about 775° F. Also within the scope of the present invention are those fuels known in the trade as residual fuels and which can be used in railroad diesel engines, power generating facilities, and the like.

The fuels of the present invention may be derived from petroleum hydrocarbons, from shales and light bituminous materials, or produced by reacting carbon monoxide and hydrogen, as in the Fischer-Tropsch synthesis. When petroleum hydrocarbons are used as the base fuel, they can be, for example, straight run, thermally, or catalytically cracked petroleum distillates, alkylates, aromatic fuels, catalytically reformed fuels, natural gasolines, hydrogenated polymers such as butene, isopentane or butane, or a blend of two or more of the above components.

As noted above, the additives of the present invention are particularly effective in reducing engine wear when high sulfur fuels are employed. It must be realized, however, that the term "high sulfur fuel" is, by its very nature, a rather flexible expression. Since the present invention includes within its scope all fuels suitable for use in both spark and combustion-ignition engines, it is apparent that what could be considered in the petroleum refining art as a high sulfur gasoline containing X weight percent sulfur could, if the same amount of sulfur were present in a diesel fuel, be considered a low sulfur diesel fuel. Thus, the sulfur content of the base fuels can vary from about 0.1 weight percent to over 2%, depending upon the type of fuel under consideration. For example, in the case of gasoline, a high sulfur gasoline could be one which contains from 0.1 to about 0.35 weight percent. In that case, the invention is particularly applicable to high sulfur gasolines having a sulfur content above about 0.15 weight percent, with gasoline base fuels having a sulfur content above about 0.25 weight percent being especially preferred. In the case of diesel fuels, a higher sulfur diesel fuel may be one containing from about 0.1 to over 2% by weight. The high sufur content diesel base fuels, that is, above about 0.5%, are especially suitable for compositions of this invention. In the case of residual fuels, sulfur contents well in excess of 2% can be found. The subject invention is particularly applicable to the reduction of wear of those residual fuels containing above about 1% sulfur,

In view of these variations, it must be understood that when the term "high sulfur fuel" is employed, the particular type of fuel (gasoline, diesel, etc.) must be considered. In any event, the fuel to which the present invention is especially applicable is an internal combustion engine fuel containing naturally occurring sulfur compounds in an amount which, under conditions of operation of the engine, normally increases appreciably the wear in said engine.

The metal sulfonates used herein may be represented by the formula:

$$(RSO_3)_xM$$

$$[(R)_aASO_3]_xM$$

wherein R is a high molecular weight cyclic, straight chain, or branched chain, saturated or unsaturated, essentially hydrocarbon radical having a molecular weight ranging from about 150 to about 800, with molecular weights of 350 to 600 of the sulfonic acid being preferred because of their more desirable solubility; A is an aromatic radical such as benzene, naphthalene, biphenyl, etc.; a is a number having a value of 1 to 4; M is a polyvalent metal selected from the group consisting of calcium and barium; and x is a number having a value equal to the valence of the polyvalent metal.

The term "essentially hydrocarbon" is intended to include radicals which are composed mainly (i.e., consist essentially) of hydrogen and carbon and which can include, in addition to hydrogen and carbon, substituents such as chlorine, bromine, oxygen, hydroxyl groups, etc., which do not substantially affect their hydrocarbon character.

More specifically, the metal sulfonates may be exemplified as dipolypropene benzene sulfonate, petroleum mahogany sulfonates, lauryl sulfonates, triacontyl sulfonates and synthetic alkyl aromatic sulfonates wherein the alkyl side chains contain from about 14 to about 20 carbon atoms.

The metal glycoxides are obtained by reacting the oxides or hydroxides of calcium or barium with glycols (i.e., vicinal alkanediols) having less than 5 carbon atoms per molecule. Suitable glycols include ethylene glycol, propane diol-1,2, butane diol 2-3, and butane diol-1,2. However, it is preferred to employ ethylene glycol.

The metallic glycoxide can be prepared and added to the particular fuel in the manner described below.

The metal oxide, or hydroxide, is dissolved in an excess of at least one of the dihydric alcohols noted above. This solution is then blended with a lubricating oil (or diesel fuel) solution of an oil-soluble metal sulfonate (preferably, the same metal as the oxide or hydroxide) described hereinbefore. The admixture thus formed is heated to remove excess dihydric alcohol, then filtered resulting in a clear, filterable fuel-soluble additive.

Although the metal oxides or hydroxides are the initial reactants, the dihydric alcohol (i.e., the vicinal alkanediol) combines therewith to form an alkaline earth metal material, which is a calcium or barium basic salt. Thus, as used herein, the alkaline earth metal material (i.e., the basic salt) means the product resulting from the reaction of the calcium or barium oxide or hydroxide and the dihydric alcohol. This alkaline earth metal material is described as glycoxide.

The product of the above-noted method of preparation is a concentrate ideally suited for inclusion in the particular fuel either at the place of the fuel manufacture or in the field. In the case of diesel fuel, it is preferred that the oil employed in forming the oil-metal sulfonate solution be one that boils within the diesel fuel boiling range. For use in gasoline, it is preferred that the oil be a lubricating oil, since the metal sulfonate will not be vaporized in the engine carburetor. The inclusion of a small amount of lubricating oil will permit the sulfonate and glycoxide to be carried through the carburetor and fuel intake system into the combustion chamber. In general, the concentrate contains from about 30 to 80 weight percent oil, and preferably, from about 40 to 60 percent by weight. In gasoline, the oil carrier should be present in an amount of from about 0.1 to 1.0 percent by weight, based on the total gasoline.

The amount of glycol used in preparing the glycoxide will depend in part upon the dihydric alcohol itself and in part upon the alkaline earth metal oxides or hydroxides which are employed. In general, the use of a low molecular weight dihydric alcohol (e.g., ethylene glycol) results in obtaining a greater amount of the basic material in the lubricating or diesel oil than the use of a higher molecular weight dihydric alcohol (e.g., propylene glycol), when both are employed in the same amounts by weight. It is preferred to select a dihydric alcohol in which the sulfonates and the alkaline earth metal oxides or hydroxides have the greatest solubility. In the formation of solutions of alkaline earth metal materials in glycols, it is beneficial to employ certain ratios by weight of the dihydric alcohol to the calcium or barium oxide or hydroxide. These ratios can vary from about 50:1 to about 2:1, 30:1 to about 10:1 being preferred.

The total amount of metals present, including the metal in the glycoxide and the metal of the sulfonate, in the fuel compositions of the subject invention is in the range of about 0.25 to about 10 millimoles per kilogram of said fuel, and the amount of metal (derived from the metallic glycoxide alone) lies in the range of from about 0.05 to about 8.0 millimoles per kilogram of fuel. It is generally preferred to employ a total metals content of from about 0.25 to about 2.5 millimoles per kilogram of fuel and from about 0.05 to about 2.0 millimoles per kilogram of fuel of metal (derived from the glycoxide alone) when the total amount of metals present is below 2.5 millimoles per kilogram of fuel.

Experimental results have shown that base ratios [i.e., the mole ratio of the alkaline earth metal (calcium or barium) present in the glycoxide to the alkaline earth metal present in the sulfonate] are considerably higher than those ratios heretofore found with alcoholates and the like, thus affording considerably more basic material for neutralizing the acids formed within the engine. In general, it has been found that the higher the base ratio, the more effective the additive. Accordingly, additives having base ratios above about 1.75 are preferred for use in the fuels of the present invention, with base ratios above about 2.5 being especially advantageous.

In addition to the aforementioned components of the fuel, agents such as pour point depressants, stabilizing agents such an anti-gum, anti-oxidizing agents, etc., may be added to the fuel. Also, in the case of gasoline, components which serve an antiknock agents such as tetraethyl lead, aromatic amines, iron carbonyl and the like, may be added to the fuel. In the case of diesel fuels, cetane-improving agents may be added. It may be desirable to employ stabilizers for the prevention of decomposition due to the presence of water, thereby increasing the storage stability of these fuels.

The following examples serve as an illustration of the effectiveness of the composition of this invention.

EXAMPLE I

A thoroughly agitated mixture was prepared containing 350 grams of a solvent-refined lubricating oil fraction of a California crude having a viscosity of 49 SSU at 210° F. and 360 SSU at 100° F. and 350 grams of calcium mahogany sulfonate (1.72 weight percent calcium; average combining weight of the free sulfonic acid about 550). To this mixture was added 20 grams of calcium oxide and 400 grams of ethylene glycol. The total mixture was heated at 300° F. for 8 hours and there-

after the unreacted ethylene glycol was removed from the product by distillation at 10 mm. pressure at 300° F. The product, stripped of excess glycol, was then filtered through a warmed filter to remove excess calcium oxide. Analysis of the lube oil-containing product showed that the calcium content was 2.36 weight percent, which is equivalent to 178% more calcium than required for combining with the sulfonic acid. This corresponds to a base ratio (the mole ratio of the calcium present in the glycoxide to the calcium present in the sulfonate) of 1.78.

To 10 gallons of a base gasoline, having the properties summarized in the table below, were added 196 grams of the above calcium glycoxide-calcium sulfonate-lubricating oil product.

Table I

INSPECTIONS OF BASE FUEL

Origin	Blend of petroleum hydrocarbons derived from California crude oil which include straight run gasoline, catalytically cracked gasoline, reformed gasoline, and an alkylate boiling in the gasoline boiling range.
Tetraethyl lead, cc.	2.7.
Sulfur content, percent by weight	0.27.
Octane Number:	
F1	91.5.
F2	83.0.
Gravity, °API	61.7.
Vapor Pressure, Reid, p.s.i.	9.3.
Distillation Range, ASTM D-86:	
Initial, °F	98.
5%	120.
10%	135.
20%	151.
30%	174.
40%	195.
50%	216.
60%	236.
70%	250.
80%	280.
90%	321.
95%	345.
End point	364.

The gasoline was tested in single-cylinder CFR valve-in-head engines having compression ratios of 6.5:1. Operating conditions during the tests were:

Coolant temperature, ° F.	100
Throttle	Full
Engine, r.p.m.	900

The engine was equipped with radioactive piston rings and wear rates were obtained by determining the rate of increase in radioactivity of the engine lubricating oil with a Geiger counter. This general method of determining wear rates is similar to the method disclosed by Messrs. P. L. Pinotti, D. E. Hull and E. J. McLaughlin in an article entitled "Harness Nuclear Fission To Measure Engine Wear" in the SAE Journal, volume 57, No. 6, June 1949, pages 52–54. The reliability of this method of determining engine wear has been ascertained by checking and correlating the results of this type of test with the same fuels in conventional tests for determining engine wear, which are characterized by long periods of engine operation and direct measurements of engine wear.

Appended drawing Fig. 1 is a graphical representation of engine data obtained during runs in which the indicated compositions were tested and wherein the above-described base gasoline was assigned a wear rate of 100%. The figure shows the beneficial effect upon engine wear realized by incorporating calcium glycoxide in the base fuel. In all of these runs the calcium concentration was maintained at 4.113 millimoles per kilogram, which is equivalent to 11.6 millimoles per gallon or 0.01645 weight percent calcium. Octane ratings made on the base fuel and on gasoline compositions containing the calcium in the various forms indicated that the octane ratings were changed less than about one number, a figure which can be considered to be within experimental error.

As can be seen from Figure 1, the compositions containing the calcium sulfonate alone (in the absence of any calcium glycoxide) actually promote ring wear in relation to the base fuel. However, it can be seen that when the calcium content is present in amounts greater than the amount of calcium present as calcium sulfonate, substantial wear reduction occurs and, further, this wear reduction is increased as the base ratio increases.

Appended Fig. 2 is a graphical representation of data obtained with the above-described CFR engines and test conditions wherein the base fuel contained both calcium glycoxide and calcium sulfonate and wherein the base ratio was 2. The figure is presented to show the effect of varying the total calcium content in gasoline compositions wherein the base fuel is the same as hereinbefore described. As can be seen, increasing the total calcium content effects further reduction in wear.

EXAMPLE II

Ethylene glycol, in an amount of 950 pounds, was charged to a 300-gallon kettle and while it was being agitated, 55 pounds of calcium oxide were sifted into the ethylene glycol over a period of 30 minutes. Thereafter 75.5 pounds of glycolic acid, which reduces the tendency of the product to gel, was charged to the kettle. Over a period of one hour, while the mixture was agitated, 680 pounds of calcium mahogany sulfonate was added to the kettle. The sulfonic acids of the sulfonate had an average combining weight of 550 and the sulfonate had a calcium content of 1.38 weight percent. A 47.5 pound quantity of a solvent-refined lubricating oil of a California crude having a viscosity of 49 SSU at 210° F. was then added. Agitation and heating of the foregoing took place for 12 hours. Thereafter, the mixture was heated slowly under a vacuum of 70 mm. Hg to 275° F., which took 9 hours. During this period unreacted ethylene glycol and water were removed by distillation. The resulting mixture was then heated to 390° F. over 2 hours accompanied by nitrogen stripping to remove the last traces of unreacted glycol. While the mixture was still hot it was filtered to remove excess calcium oxide. Analysis of the product showed that it had a total calcium content of 4.06 weight percent, of which 1.06 weight percent calcium is present as calcium sulfonate. That is, a total of 3 weight percent of the total product was calcium that was uncombined with the neutral calcium sulfonate. This is equivalent to a base ratio of 2.83.

To each gallon of diesel fuel, inspections of which are shown in Table II, 8.04 grams of the above calcium glycoxide-calcium sulfonate-lubricating oil product were added to form the composition which was tested as indicated below.

Table II

Sulfur, lamp, percent	1.05
Cetane number	43.5
Viscosity, SSU, at 100° F.	38.0
Gravity, ° API	34
Distillation, ASTM D-158:	
Start, ° F.	370
10%	458
50%	533
90%	620
End point	704

The tests were conducted in a single-cylinder Caterpillar diesel engine operated under the following conditions:

Jacket temperature, ° F.	150
Sump temperature, ° F.	150
Exhaust temperature, ° F.	800
Rated load, percent	100

The engine was equipped with radioactive piston rings and the wear rates were obtained in an identical manner as in the preceding example.

The above-described base diesel fuel was assigned a wear rate of 100. The radioactivity test found that when the total calcium content was 2.5 millimoles per kilogram or 0.01 weight percent calcium, that wear was reduced 24% over the base fuel. Additionally, inspections of the engine showed that there were substantially no deposits on the injector tips, whereas when the base diesel fuel was used without the additive of the present invention, deposition was comparatively heavy.

Tests conducted with a Cummins HB 600 engine at 1200 r.p.m. and under 10 percent weighted load indicated that the consumption of the fuel containing the calcium glycoxide was constant over a test period of 100 hours, whereas the consumption of the base fuel, that is, without the additive of the present invention, constantly increased during the entire test period. This latter test indicates that the calcium glycoxide-containing diesel fuel was consumed evenly during the test due to the absence of injector tip deposition. It was found further that when other calcium additives such as calcium naphthenate and calcium cetyl phenate were added in similar concentrations, the specific fuel consumption increased markedly during the test period, indicating that the calcium itself was not the primary factor in reducing deposition. Additionally, the smoke percentage during the test followed a similar pattern in that during the tests in which the calcium sulfonate-calcium glycoxide was used, the smoke rate was substantially constant during the entire test. On the other hand, when calcium cetyl phenate or calcium naphthenate were added to the base fuel, a considerable increase in smoking occurred during the test. This latter observation was also noted in the case where the base fuel without additives was tested.

EXAMPLE III

Neutral barium mahogany sulfonates, prepared by converting sodium sulfonate to barium sulfonate in the presence of barium oxide, were added to the base diesel fuel of Example II in a concentration, based upon barium, of 4.113 millimoles of barium per kilogram of fuel. An average of engine tests conducted in a manner and under the conditions described in Example II above, gave a wear rate of 130%. With the base fuel having a wear rate of 100%, this shows that compositions containing only barium sulfonate and no barium glycoxide, not only were ineffective for reducing wear, but actually promoted wear.

EXAMPLE IV

A mixture was prepared containing 350 grams of a solvent-refined lubricating oil from a California crude having a viscosity of 435 SSU at 100° F. and 49 SSU at 210° F., and a sulfonated fraction of a California crude which had been extracted with hexanes and which contained 17% free sulfonic acids having an equivalent weight of about 500. This mixture was stripped of hexane in a vacuum distillation unit maintained at a temperature of about 70° C. and 3 mm. Hg pressure. The hexane-free mixture was found to weigh 620 grams. The mixture was placed in a two-liter, three-necked round bottom flask fitted with a condenser. To this flask was added 126 grams of barium hydroxide octahydrate. The mixture was heated and constantly agitated until all water had been removed by distillation. This latter operation was done under a slight vacuum and at a pot temperature of about 175 to 180° C. for 2 hours after all evidences of water had been removed. The total time required was between 4 and 6 hours. After the conversion of the sulfonic acids had been completed by the above heating, the mixture was filtered while hot (150° C.) through clay, and yielded 580 grams of product which contained 7.84% barium. Analysis of this product showed that approximately 3.92% of the barium was present as barium hydroxide and 3.92% of the barium was present as barium sulfonate. This is equivalent to a base ratio of 1:1.

To 15 gallons of the base gasoline shown in Example I, 306 grams of the barium hydroxide-barium sulfonate-lubricating oil product were added to form the composition which was tested according to the procedure described in Example I above. An average of results indicated that this composition reduced the wear 53% over the wear (100%) that occurred when the base fuel alone was employed. In this test, the total barium concentration was maintained at 4.113 millimoles per kilogram, which is equivalent to 11.6 millimoles per gallon or 0.056 weight percent barium.

When the barium content of the barium hydroxide was increased to 56% of the total barium present (accomplished by increasing the amount of barium hydroxide octahydrate), wear reduction was further increased to an average of 68%.

From the series of tests, it is evident that the compositions containing barium hydroxide gave wear reductions whereas in the presence only of barium sulfonate (see Example III) wear promotion actually occurred. Thus, it can be seen that base ratios of only one will reduce wear and that further wear reduction will result when the base ratio (that is, when the barium hydroxide concentration is increased) is above that figure.

EXAMPLE V

This example illustrates that the use of ethylene glycol to form the barium glycoxide will give considerably higher base ratios than when water or alcohols are used to form the hydroxide or alcoholates.

In this example, basic barium sulfonates were prepared employing ethylene glycol, water, methanol and n-butanol as solvents. In each case, 100 grams of a neutral barium sulfonate containing 4.88 percent total barium and 4.7 percent barium as sulfonate (prepared by contacting calcium sulfonate derived from a solvent-refined California waxy lubricating oil in a thinner solution with an aqueous $BaCl_2$ solution, washing with water and stripping out the thinner) and 25 grams of a California naphthenic base oil having a viscosity of about 300 SSU at 100° F. were charged to a 500 ml., 3-necked flask (equipped with a mechanical stirrer and a thermometer) and heated to about 275°–300° F. In these solutions wherein the solvent was (1) ethylene glycol and (2) water, 35 grams of $Ba(OH)_2 \cdot 8H_2O$ in 75 grams of solvent were added slowly over a period of about 10 minutes to the hot sulfonate-oil mixture, reducing the temperature of the latter to 210°–260° F., depending upon the solvent employed. In the case where methanol was the solvent, about 95 grams of a methanol were required to dissolve the $Ba(OH)_2 \cdot 8H_2O$, but in all other respects, the procedure was the same as that using glycol. When n-butanol was employed as the solvent, it was found necessary to add the 35 grams of solid

$$Ba(OH)_2 \cdot 8H_2O$$

and 75 grams of n-butanol separately (but at the same time) because of the poor solubility of $Ba(OH)_2 \cdot 8H_2O$ in the alcohol.

In all cases the reaction mixtures (described above) were stirred for 1–2 hours during which time the temperature was gradually increased. In the water and glycol products, the temperature was raised to about 270°–290° F. The methanol and n-butanol reaction mixtures were refluxed at their boiling points for about 3 hours.

The four reaction mixtures were then evaporated of solvent and heated to 360° F. at atmospheric pressure, cooled to about 300° F. and vacuum stripped to 360° F. and 5–10 mm. Hg pressure. Finally, the mixtures were filtered through celite.

The base ratios found in the above reaction mixtures are summarized in Table III below.

Table III

Solvent	Product		
	Percent Ba as Sulfonate	Percent Ba as Base	Base Ratio
Ethylene Glycol	3.33	9.10	2.72
Water	3.67	4.26	1.19
Methanol	3.92	5.73	1.46
n-Butanol	5.01	3.02	0.60

From the above tabulation of experimental results, it can be seen that the base ratio attained by the use of ethylene glycol is far higher than that realized by any of the other solvents. Further, this high base ratio must be compared with those alcohols giving the hightest ratio, since it has been found that the reaction of alcohols with metals to yield alcholates increases in difficulty from primary, secondary to tertiary alcohols. That is, primary alcohols react most easily with the metals.

Of further interest is the fact that the amount of $Ba(OH)_2 \cdot 8H_2O$ employed, 35 grams, would add enough barium as base to bring the base ratio up to a theoretical 3.2 if this amount could be incorporated in the barium sulfonate. It can be seen that the glycoxide of the present invention is the only compound that approaches such a ratio.

EXAMPLE VI

This example illustrates that, like the case of barium, the calcium glycoxide attains a considerably higher base ratio than when alcohol or water or mixtures thereof are employed as the solvent. The experimental results upon calcium, conducted in a manner similar to that of barium shown in Example V, are summarized in Table IV.

Table IV

Experiment No.	Sulfonate		Base		Solvent		Temp., °F.	Time, hrs.	Product	
	Gms.	Percent Ca	Type	Gms.	Type	Gms.			Percent Ca	Base Ratio
130-15B	700	0.86	CaO	20	Ethylene Glycol	400	300	8	2.36	1.74
130-30	800	0.55	CaO	21	do	400	300	3	1.90	2.45
130-14A	530	1.16	CaO	8.6	Ethanol	200	Reflux	12	1.60	0.38
484-17.3	400	0.80	CaO	5	50% Ethanol + 50% H_2O	100	do	10	.95	0.19
484-17.2	400	0.80	CaO	5	50% Methanol + 50% H_2O	100	do	10	1.02	0.28
484-17.1	400	0.80	CaO	5	H_2O	50	210	10	1.01	0.26

This application is a continuation-in-part of our co-pending applications Serial No. 268,116 (Barusch) and No. 268,117 (Barusch and Pinotti), both filed on January 24, 1952, and now both abandoned.

We claim:

1. A hydrocarbon fuel composition comprising a major proportion of normally liquid hydrocarbons, a minor proportion of at least one alkaline earth metal glycoxide selected from the group consisting of barium and calcium glycoxides, and a minor proportion of at least one oil-soluble alkaline earth metal sulfonate derived from a sulfonic acid of a molecular weight range from about 150 to about 800 and selected from the group consisting of barium and calcium sulfonates, said minor proportions of alkaline earth metal glycoxides and sulfonates providing in the fuel composition a total metal content from about 0.25 to about 10.0 mM./kg., of which metal content from about 0.05 to about 8.0 mM./kg. is the metal of the glycoxide, the mol ratio of the metal present in glycoxide to the metal present in sulfonate being above about 1.75.

2. The fuel composition of claim 1 wherein the normally liquid hydrocarbons boil within the gasoline boiling range.

3. The fuel composition of claim 1 wherein the normally liquid hydrocarbons boil within the diesel fuel boiling range.

4. A hydrocarbon fuel composition suitable for use in an internal combustion engine and comprising a major proportion of normally liquid hydrocarbons containing naturally occurring sulfur compounds in an amount which normally increases wear in said engine during operation, a minor proportion of at least one alkaline earth metal glycoxide selected from the group consisting of barium and calcium glycoxides, and a minor proportion of at least one oil-soluble alkaline earth metal sulfonate derived from a sulfonic acid of a molecular weight range from about 150 to about 800 and selected from the group consisting of barium and calcium sulfonates, said minor proportions of alkaline earth metal glycoxides and sulfonates providing in the fuel composition a total metal content from about 0.25 to about 10.0 mM./kg., of which metal content from about 0.05 to about 8.0 mM./kg. is the metal of the glycoxide, the mol ratio of the metal present in glycoxide to the metal present in sulfonate being above about 1.75.

5. A high sulfur hydrocarbon fuel composition comprising a major proportion of normally liquid hydrocarbons containing at least 0.1% by weight of sulfur in the form of naturally occurring sulfur compounds, a minor proportion of at least one alkaline earth metal glycoxide selected from the group consisting of barium and calcium glycoxides, and a minor proportion of at least one oil-soluble alkaline earth metal sulfonate derived from a sulfonic acid of a molecular weight range from about 150 to about 800 and selected from the group consisting of barium and calcium sulfonates, said minor proportions of alkaline earth metal glycoxide providing in the fuel composition from about 0.05 to about 8.0 mM./kg. of metal, and said alkaline earth metal sulfonates providing in the fuel composition from about 0.2 to about 2.0 mM./kg. of additional metal, the mol ratio of the metal present in glycoxide to the metal present in sulfonate being above about 1.75.

6. The fuel composition of claim 5 wherein the normally liquid hydrocarbons boil within the gasoline boiling range and contain at least 0.15 percent by weight of sulfur in the form of naturally occurring sulfur compounds.

7. The fuel composition of claim 5 wherein the normally liquid hydrocarbons boil within the diesel fuel boiling range and contain at least 0.5 percent by weight of sulfur in the form of naturally occurring sulfur compounds.

8. The fuel composition of claim 5 wherein the glycoxide and sulfonate are both calcium.

9. The fuel composition of claim 5 wherein the glycoxide and sulfonate are both barium.

10. An additive concentrate intended for incorporation into a normally liquid hydrocarbon fuel which com-

prises from about 30 to 80 percent by weight of a normally liquid hydrocarbon carrier boiling in the diesel fuel boiling range, a metal present in the form of at least one alkaline earth metal glycoxide selected from the group consisting of barium and calcium glycoxides, said glycoxide being present in an amount sufficient to provide from about 0.05 to about 8.0 millimoles of metal per kilogram of fuel, and a metal present in the form of an oil-soluble alkaline earth metal sulfonate selected from the group consisting of barium and calcium sulfonates, said sulfonate being present in an amount sufficient to provide from about 0.2 to about 2.0 millimoles of additional metal per kilogram of fuel, the mol ratio of the metal present in glycoxide to the metal present in sulfonate being above about 1.75.

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