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HYDROCARBON OIL COMPOSITIONS

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The present invention relates to novel hydrocarbon compositions and to a method of their utilization in the treatment of cellulose gasket materials.

Cellulose gaskets, especially paper gaskets, have been used for years to seal joints of metal containers for hydrocarbon liquids. Such gaskets are almost universally used, for example, to seal the flanges of automotive carburetor float bowls, to seal clean-out plugs, filters and outlet pipes of automotive fuel tanks and the like. In all of these applications the gasket material must have sufficient flexibility and compressibility to conform to the irregularities of the surfaces of the joint. This requirement in turn necessitates a certain amount of porosity. Paper and other cellulose materials have this requisite porosity. However, because such materials are fibrous, they facilitate a "wicking" action by which liquids leak through the gasket. This, of course, defeats the purpose of the gasket. In the case of low surface-tension liquids, such as hydrocarbons, and especially gasoline, this wicking action is a particularly serious problem. Striking evidence of this can be seen on the external surfaces of the carburetor of nearly any automobile. The red or orange dye of the gasoline is deposited on these surfaces, in admixture with gum and other relatively non-volatile constituents of the gasoline, in direct proportion to the amount of gasoline which leaks through the carburetor bowl gasket and evaporates. In many cases the leakage is so great that the gummy residue of evaporated gasoline collects on the external linkages, for example, on the automatic choke and, on some cars, on the starter switch, causing sticking of these mechanisms, and leading to stalling, poor gasoline mileage, and similar troubles.

A usual method of inhibiting the leakage of hydrocarbon oils through cellulose gaskets is to impregnate the gasket material with a combination of glue and glycerine. A gasket cut from material treated in this manner is considerably improved, but the treatment is only temporarily effective and gasoline or other hydrocarbons will soon leak through. This is perhaps because of the leaching action of the hydrocarbon on the glycerine and the oxidation hardening and cracking of the glue.

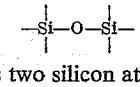
A principal object of the present invention is to provide hydrocarbon compositions with decreased tendencies to leak through cellulose gaskets. A further object of the invention is to provide a method of inhibiting the leakage of hydrocarbon liquids through cellulose gaskets. Another object is to provide an improved method of treating a cellulose gasket material to render it less permeable to hydrocarbon liquids. Another object is to provide an improved gasket composition with more permanent sealing qualities. Other objects of the invention will appear in the description of the invention.

It has now been discovered that hydrocarbon liquids with average boiling points below about 600° F., and especially liquid fuels such as gasolines, are improved to have less tendency to leak through cellulose gaskets by the incorporation therein of a combination additive consisting essentially of certain proportions of a hydrocarbyl polysiloxane and of an organic phosphorus compound. The leakage of the hyrocarbon through a cellulose gasket, especially in the case of gasoline, may thereby be reduced to as little as 10 to 15% of the leakage before the incorporation of the additive.

It has also been found that the use of the hydrocarbon compositions of the invention, that is, those containing certain proportions of the hydrocarbyl polysiloxane and organic phosphorus compound additive renders any cellulose gasket with which they come in contact permanently less permeable to hydrocarbon liquids, even to hydrocarbon liquids not containing the combination polysiloxane-phosphorus compound additive. Heretofore, a leaking gasket would have to be replaced, for example, by a gasket impregnated with glue and glycerine, for some temporary relief or by a relatively expensive synthetic rubber gasket or the like. One of the great advantages of the present invention, therefore, is that the necessity for gasket replacement, with attendant labor and material costs, is avoided, because by the use of the hydrocarbon compositions of the invention the gasket is rendered substantially leak-proof during its actual use.

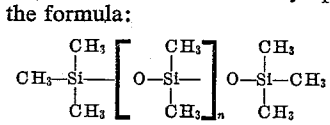
A further aspect of the invention is that cellulose gasket material which is impregnated with the combination of the hydrocarbyl polysiloxane and the organic phosphorus compound is eminently suitable for the manufacture of gaskets for hydrocarbon systems. Thus, regardless of whether a hydrocarbon liquid contains the polysiloxane-phosphorus compound combination additive of the invention or not, it will be retained more effectively by the gasket compositions of the invention.

Although the nomenclature of polymeric silicon compounds is not entirely well settled, it is generally accepted that a polysiloxane is a compound which contains the structural group



A disiloxane contains two silicon atoms, a trisiloxane contains three, etc. The hydrocarbyl polysiloxanes of the present invention contain hydrocarbyl group to silicon atom (R/Si) ratios of from about 1.7 to 3.0. They can be divided generally into two types.

The first type consists of the so-called "silicone fluids." These compounds are generally straight-chain linear polysiloxanes having terminal silicon atoms to which are attached three hydrocarbyl groups and with two hydrocarbyl groups attached to each of the other silicon atoms. However, they can also be unbranched cyclic polysiloxanes with two hydrocarbyl groups attached to every silicon atom. The R/Si ratios of such compounds can vary from about 2.0 (for a very long chain) to 3.0 (for the compound hexamethyl disiloxane). However, they are ordinarily referred to in the art as dihydrocarbyl polysiloxanes because in all but the lower members of the series the R/Si ratio is quite close to 2. The silicone fluids are preferred for the purposes of the present invention. A common type of such compounds, and one which is particularly preferred, consists of the dimethyl polysiloxanes, which have the formula:



wherein n can vary from 0 to 2000 or more. The viscosity of the silicone fluids is determined by the average chain length, and in the present invention, can vary from 0.65 centistoke at 25° C. (the viscosity of the lowest member of the dimethyl polysiloxanes, hexamethyl disiloxane) to as high as 60,000 centistokes or more at 25° C. However, it is preferred that the viscosity be at least 10 centistokes

and more especially at least 100 centistokes. A viscosity of from 500 to 30,000 centistokes, such as 12,500 centistokes, has been found to be especially effective.

The second type of the hydrocarbyl polysiloxanes of the invention consists of the so-called partially condensed "silicone resins." These compounds are well-known and are commercially available, usually in the form of solutions in solvents such as toluene or xylene. They can be used for the purposes of the invention either in such solutions or in the pure form. The partially condensed silicone resins are compounds which probably contain a number of hydroxyl groups attached to the silicon atoms of the silicon-oxygen chains, which groups make possible further condensation of the molecules by crosslinking between the chains. The R/Si ratio determines the extent to which crosslinking can occur. Heretofore, these materials have been useful generally only after evaporating the solvent and completing the condensation process (i. e., "curing") to produce resinous solids, by baking or some other heating process and usually in the presence of a catalyst. They have been used in the solid form as electrical insulation material, molding resins, release agents, concrete, and masonry coating materials, and the like. However, such applications will ordinarily require R/Si ratios of less than 1.7 because resins of higher R/Si ratios cure only with the application of very high temperatures over extended periods of time. With the phosphorus compounds described below the partially condensed resins of R/Si ratios of 1.7 to 2 effect the objects of the present invention without any curing process and they are used in the same manner as are the silicone fluids.

The term "partially condensed" would literally include all resins which are capable of further condensation to some degree, however slight. However, in commercial usage it is generally understood that the term refers to those resins in which the degree of crosslinking has not reached the point at which the resin becomes substantially insoluble (i. e., less than about 1% by weight) in solvents such as toluene or benzene. It is in such a sense that the term will be used herein, because for the purposes of the present invention the resins must not only have an R/Si ratio of at least 1.7, but they must also have a degree of crosslinking no greater than would render them less soluble in toluene or xylene than about 1% by weight.

The hydrocarbyl groups of both the silicone resins and the silicone fluids are generally lower hydrocarbyl groups, i. e., those containing from 1 through 7 carbon atoms. Of such hydrocarbyl groups the lower acyclic alkyl groups, for example, methyl, ethyl, propyl, butyl, and amyl groups, are preferred, especially methyl and ethyl groups. However, polysiloxanes containing lower cyclic hydrocarbyl groups, for example, phenyl, benzyl, and cyclohexyl groups, are also within the scope of the invention. Polysiloxanes containing mixtures of such lower hydrocarbyl groups are also effective, particularly methyl phenyl polysiloxanes in which the ratio of methyl to phenyl groups is at least 1:1.

The requirement that the silicon atoms of the silicon-oxygen chains of both the silicone resins and the silicone fluids be substantially completely substituted with hydrocarbyl groups or hydroxyl groups is a matter of resistance to oxidation, hydrolysis and chemical reaction. The silicon compound can function properly in accordance with the purposes of the invention only if it will remain chemically unreactive toward the cellulose and the various components of the hydrocarbon liquid, particularly such as olefins, tetraethyl lead, halohydrocarbon scavengers, dyes, oxidation inhibitors, detergents, rust inhibitors, traces of water and dissolved air, and the many other components one encounters in present day commercial gasoline, kerosene, diesel fuel and the like. Of course, the silicon compound should not react with metal to form deleterious products which might corrode or foul the containers or equipment with which the hydrocarbon composition comes in contact. For example, the polysiloxanes of the present invention should be clearly distinguished from conventional organo-silicon "water-proofing agents," such as the methyl silicon halides of U. S. 2,306,222, which are also used as resin intermediates, for several reasons. The halide atoms of such compounds are extremely reactive and hydrolyze in the presence of moisture or react with the hydroxy groups of cellulose, in either case with the evolution of hydrochloric or other hydrohalic acid. Of course, such compounds are not suitable in hydrocarbon compositions, such as gasolines, which will normally contain traces of water. Also, a treatment of a cellulose material with such compounds requires a neutralization step, for example, with ammonia, to avoid the disintegration of the cellulose. The method of the present invention eliminates this. Even more important, however, is the distinction that the present invention is concerned with the resistance of the gasket material to the passage of hydrocarbon rather than water. It should also be mentioned that polysiloxanes which contain halogen atoms in the hydrocarbyl groups are not suitable for the purpose of the present invention. It is preferred that the hydrocarbyl groups of the silicone fluids of the invention contain no non-aromatic unsaturation.

As heretofore mentioned, a hydrocarbon-soluble organic phosphorus compound is also essential to the compositions and methods of the present invention. This component can be a phosphine, phosphine oxide, phosphite, phosphonite, phosphinite, phosphate, phosphonate, phosphinate or a sulfur analogue thereof. The organic radical or radicals of the phosphorus compound can be alkyl (acyclic or alicyclic) or aryl. They are preferably hydrocarbyl radicals (that is, radicals containing only carbon and hydrogen atoms) and especially cyclic hydrocarbon radicals. However, if desired, any one radical may also contain a halogen atom, in which case the halogen atom is preferably chlorine or bromine, and especially chlorine. Of the cyclic radicals, hydrocarbyl-substituted cyclic radicals and especially polyhydrocarbyl-substituted cyclic radicals are preferred. Phosphorus compounds having radicals containing up to 10 carbon atoms are most useful, and it is preferred that the radicals contain at least 5, and especially at least 5 carbon atoms. It is also preferred that the phosphorus compound contain no sulfur. Particularly suitable are the trihydrocarbyl phosphates.

Thus, suitable phosphorus compounds for the practice of the invention are those having the formula:

$$P(X)_a(XR)_b(R)_c$$

where:

X is an oxygen or sulfur atom, that is, a chalcogen atom having an atomic number from 8 to 16, inclusive;

R is a monovalent radical containing no atoms other than carbon, hydrogen, and halogen, no more than one halogen atom, and from 1 to 10 carbon atoms;

a Is a whole number from 0 to 1, inclusive;

b And *c* are whole numbers from 0 to 3, inclusive, the sum of *b* and *c* being equal to 3.

Typically suitable for the purposes of the invention are the following exemplary specific compounds: tricresyl phosphate, triamyl thionophosphate, triphenyl phosphine, trimethyl phosphine oxide, tributyl phosphite, tris(2-propyl) phosphite, bis(2-propyl) 2-propylphosphonate, phenyl dimethylphosphinate, propyl dicresyl thiolophosphate, tris(3,3,5-trimethylcyclohexyl) phosphate, tris(2-chloropropyl) thionophosphate, diphenyl cresylphosphonite, dimethyl xylyl phosphate, and ethyl dimethylthiophosphinite.

The relative proportions of the phosphorus compound and the hydrocarbyl polysiloxane are important to the invention. In general, the weight ratio of the phosphorus compound to the silicon compound should be 10:1 or more and no greater than 1000:1, preferably at least 30:1 and up to 500:1.

The concentrations of the phosphorus compound and the silicon compound in the hydrocarbon compositions of the invention can be extremely small and can vary over a wide range, because as the hydrocarbon compositions penetrate the gasket material there is a cumulative effect which eventually results in an equilibrium at a greatly reduced permeability. Of course, a sufficient amount of the additive should be present to reach this equilibrium in a reasonable time. Therefore, it is preferred that the silicon compound be present in an amount at least 0.00001% by weight of the hydrocarbon and the phosphorus compound at least 0.001% by weight of the hydrocarbon. More especially, beneficial results will be quickly obtained when the concentration of the silicon compound is about 0.0001% by weight or more and the concentration of the phosphorus compound is at least 0.01% by weight. On the other hand, depending upon the ultimate use to which the hydrocarbon composition is to be put, the concentrations must not be too great. For example, hydrocarbon fuel compositions should in general contain no more than about 0.05% by weight, preferably not more than 0.005% by weight and still better no more than 0.001% by weight silicon compound, and no more than about 1%, especially not more than 0.1% by weight, and preferably no more than 0.07% by weight phosphorus compound, because larger concentrations will result in deleterious side effects during the combustion process. Particularly preferred ranges are from about 0.0001 to about 0.0005% by weight of the silicon compound and from about 0.02 to about 0.06% by weight of the phosphorus compound.

The gasket compositions of the invention should contain the silicon compound and the phosphorus compound within the above-mentioned weight ratio ranges. Additionally, the concentration of the silicon compound in the gasket material should be generally at least about 0.005% by weight (based on the weight of dry gasket material) and preferably at least about 0.05% by weight. Also the full benefits of the invention are obtained at silicon compound concentrations no more than about 5% by weight. Preferably 1% by weight or less should be used. Concentrations of the silicon compound in the range of 0.1 to 0.5% and particularly about 0.2% by weight are especially effective. The concentration of the phosphorus compound in the gasket composition should be at least 0.1% by weight (based on the weight of dry gasket material) and preferably at least 2% by weight. Also no more than 50% by weight is necessary and preferably 20% by weight or less should be used. Concentrations of the phosphorus compound in the range of 5 to 15% and particularly about 10% by weight are especially effective.

It has been found that there is a cooperative action between the silicon compound and the phosphorus compound in the present compositions and methods. Both of these components must be present in order to obtain the benefits of the invention and furthermore the simultaneous presence of these components eliminates certain disadvantages of the presence of either component alone. The following experiments and examples are set forth only to exemplify the invention and to illustrate the interaction of the silicon compound and phosphorus compound and not to limit the scope of the invention. Further extensions of the invention are clearly suggested as will be understood by those versed in the art.

Experiments Nos. 1 through 4, below, show the extent to which a gasket paper treated with a phosphorus compound alone becomes less pervious to gasoline:

EXPERIMENT NO 1

The gasket paper of this and the following experiments is a type typically used as standard equipment in the carburetor float bowl gaskets of current-model U. S. automobiles and trucks. This is an untreated high strength Manila saturating type, predominantly kraft with minor amounts of sulfite, rag and jute stocks. It is substantially all cellulose.

A strip of this gasket paper, 1 by 6 inches, was totally immersed in a solution of 9.3 grams of tributyl phosphite in 100 cc. of benzene, removed and dried by evaporation at room temperature. The strip was then clamped between two 1 by 6 inch pieces of plate glass and the pressure on the paper was adjusted to a standard set for all of these experiments by means of a precision torque wrench. One end of this assembly was immersed to a depth of 1 inch in gasoline. The criterion for the susceptibility of the paper to gasoline permeability was the time interval before the paper became wetted with gasoline to a height of 10 centimeters above the level of the gasoline in which the assembly was immersed. For convenience this criterion will be referred to hereinafter as the "10 cm. rise time" and whenever this term is used the value will be understood to have been obtained in exactly the same manner as described above except for expressed deviations.

In the present experiment with tributyl phosphite the 10 cm. rise time was 12 minutes. When the experiment was repeated with no pretreatment of the paper, the 10 cm. rise time was 11 minutes. Thus the pretreatment with tributyl phosphite effected an increase in 10 cm. rise time of 1 minute.

EXPERIMENT NO. 2

A pretreatment of the gasket paper with a solution of 10.0 grams of triphenylphosphine in 100 cc. of benzene resulted in a 10 cm. rise time of 13 minutes; that is, an increase of 2 minutes.

EXPERIMENT NO. 3

A pretreatment of the gasket paper with a solution of 11.8 grams of tricresyl phosphate in 100 cc. of benzene resulted in a 10 cm. rise time of 22 minutes; that is, an increase of 11 minutes.

EXPERIMENT NO. 4

A pretreatment of the gasket paper with a solution of 10.0 grams of tris(3,3,5-trimethylcyclohexyl)phosphine in 100 cc. of benzene resulted in a 10 cm. rise time of 17 minutes; that is, an increase of 6 minutes.

In addition to the fact that the above benefits are relatively small, a phosphorus compound as the sole impregnant of a gasket in actual service would soon be leached out by the hydrocarbon and these benefits would disappear. Furthermore, even if a gasoline composition containing such phosphorus compounds were used in order to replace the impregnant lost by the leaching action of the gasoline, still another disadvantage would be present. The gasoline which would leak through the gasket would contain the phosphorus compound and this would concentrate in the heavy ends of the gasoline upon evaporation. The heavy ends would then have a lower average volatility and tend to remain in a mobile fluid or semi-fluid form. This would then defeat one of the important purposes of the present invention, namely, the elimination of any sticking of external carburetor linkages due to the accumulation of tars, gums, etc. from leaking gasoline.

EXPERIMENT NO. 5

A pretreatment of the gasket paper of Experiments Nos. 1 through 4 with a solution of 0.13 gram of a dimethyl polysiloxane fluid with a viscosity of 100 centistokes at 25° C. in 100 cc. of benzene resulted in a 10 cm. rise time of 11 minutes. Thus, by comparison with the 10 cm. rise time of 11 minutes obtained without any pretreatment of the gasket paper, it can be seen that the silicone treatment alone was totally ineffective to change the 10 cm. rise time.

EXPERIMENT NO. 6

A pretreatment of the gasket paper with a solution of 0.13 gram of the silicone fluid of Experiment No. 5

together with 9.3 grams of tributyl phosphite in 100 cc. of benzene resulted in a 10 cm. rise time of 16 minutes; that is, an increase of 5 minutes. This should be compared with the increase of 1 minute in Experiment No. 1 and the total ineffectiveness of the treatment with silicone fluid alone in Experiment No. 5.

EXPERIMENT NO. 7

A pretreatment of the gasket paper with a solution of 0.13 gram of the same silicone fluid together with 10.0 grams of triphenylphosphine in 100 cc. of benzene resulted in a 10 cm. rise time of 20 minutes; that is, an increase of 9 minutes. This should be compared with the increase of 2 minutes in Experiment No. 2 and the total ineffectiveness of the treatment with silicone fluid alone in Experiment No. 5.

EXPERIMENT NO. 8

A pretreatment of the gasket paper with a solution of 0.13 gram of the same silicone fluid together with 11.8 grams of tricresyl phosphate in 100 cc. of benzene resulted in a 10 cm. rise time of 30 minutes; that is, an increase of 19 minutes. This should be compared with the increase of 11 minutes in Experiment No. 3 and the total ineffectiveness of the treatment with silicone fluid alone in Experiment No. 5.

EXPERIMENT NO. 9

A pretreatment of the gasket paper with a solution of 0.13 gram of the same silicone fluid together with 10.0 grams of tris(3,3,5-trimethylcyclohexyl)phosphine in 100 cc. of benzene by the procedure of Experiment No. 1 resulted in a 10 cm. rise time of 20 minutes; that is, an increase of 9 minutes. This should be compared with the increase of 6 minutes in Experiment No. 4 and the total ineffectiveness of the treatment with silicone fluid alone in Experiment No. 5.

The above experiments prove the effectiveness of the gasket treatment with the combination of silicon compound and phosphorus compound by actual transfer of the components from a relatively concentrated solution thereof. The next series of experiments was designed to determine the possibility of a treatment of the gasket during actual use with the hydrocarbon compositions to be confined by the gasket and containing the necessarily minor concentrations of silicon compound and phosphorus compound. In order to simulate as accurately as possible the actual environmental factors encountered in the practical use of a gasket, and yet to conduct the testing under controlled laboratory conditions, a "mock-up" of a carburetor float bowl and gasket was assembled. This equipment comprised a machine-faced flanged cylindrical gasoline chamber of the usual carburetor "pot metal," a 95% zinc die casting alloy (in this case, "Zamack 5"). The flanges (and the gaskets used in the tests) measured 3" O. D. and 2⅛" I. D. The flanges with the gasket between them were clamped together in a horizontal position by means of spring loaded steel "back-up" flanges in such a manner as to provide a constant and evenly distributed force on the gasket of a magnitude of about 57 lbs. per square inch, typical of that encountered in normal automotive service. Air streams were directed against the exposed outside edge of the gasket between the flanges at a rate sufficient to provide an air circulation comparable to that obtained around a carburetor float bowl in an automobile traveling about 40 to 50 miles per hour.

Each test was made with the gasoline chamber completely full of the gasoline composition to be tested. However, the pressure in the gasoline chamber at the inner edge of the gasket was adjusted to atmospheric pressure by means of a liquid connection from the bottom of the chamber, through a U-tube, to a burette. The height of the burette was adjusted throughout the test as the gasoline leaked through the gasket, so as to maintain the level of the gasoline in the burette at the same height as the gasket. The pressures on the inside and outside edges of the gasket were therefore equal, thus avoiding leakage due to pressured flow, and also exactly duplicating the conditions of a vented carburetor float bowl. The loss of gasoline by leakage through the gasket was determined by the change in the burette reading over timed periods.

EXPERIMENT NO. 10

The gasoline composition used in this test was a commercial gasoline of the normal boiling range containing 1.75 cc. of tetraethyl lead per gallon, 1.0 theory of ethylene dichloride, 0.5 theory of ethylene dibromide, 0.0004% by weight of N,N'-disecondarybutylparaphenylene diamine (an oxidation inhibitor), 0.0001% by weight of disalicylalpropylenediamine (a metal deactivator) and dye. The gasket material used was the same as that of Experiments Nos. 1 through 9 and was installed in the carburetor float chamber mock-up as received, that is, without any impregnation or other physical or chemical treatment. The gasoline leakage rate through the gasket was determined in accordance with the above-described procedure. The rate levelled out at 5.6 milliliters per hour. This equilibrium rate remained constant (±0.1 ml. per hour) for 95 hours, at which time the test on this gasoline was discontinued.

EXPERIMENT NO. 11

Tricresyl phosphate and a dimethyl polysiloxane fluid of 500 centistokes viscosity at 25° C. was added to the gasoline of Experiment No. 10, the former to a concentration of 0.65 gram per gallon (0.023% by weight) and the latter to a concentration of 0.014 gram per gallon (0.0005% by weight). The test was continued with the same gasket used in Experiment No. 10 and without removing it from the equipment. The gasoline leakage rate decreased immediately and within 75 hours levelled off to a rate of 0.8 ml. per hour. This equilibrium rate remained constant (±0.05 ml. per hour) for 115 hours, at which time the test on this gasoline was discontinued. The combination additive of the present invention therefore decreased the leakage rate to 14% of the value without the additive.

EXPERIMENT NO. 12

In order to determine the permanency of the decrease in permeability of the gasket of Experiments Nos. 10 and 11, the gasoline of Experiment No. 11 (containing the phosphorus compound and the silicone fluid) was replaced by the gasoline of Experiment No. 10 (containing neither phosphorus compound nor silicone fluid). Again the gasket was not disturbed. The gasoline leakage rate was still 0.8 ml. per hour even after 325 hours, at which time the test was discontinued.

Road Tests

An extensive series of road tests was undertaken to prove the benefits of the invention under actual operating conditions. Over 50 automobiles of popular makes participated in these tests. Over 100,000 miles of driving was accumulated and the tests were made in both winter and summer weather, with both "stop-and-go" city and high-speed highway driving, and in several different parts of the United States. In every case the gasoline compositions of the invention reduced the leakage of gasoline through the carburetor gaskets, and this benefit was obtained without disturbing the gasket in any way, and with no tightening or other adjustment of the hold-down bolts or other parts.

Typical compositions particularly suitable for the practice of the invention are as follows:

EXAMPLE I

An automotive gasoline composition containing 0.03% by weight tricresyl phosphate and 0.0005% by weight

dimethyl polysiloxane fluid of a viscosity at 25° C. of 500 centistokes.

EXAMPLE II

A diesel fuel composition containing 0.05% by weight tributyl phosphite and 0.005% by weight dimethyl polysiloxane fluid of a viscosity at 25° C. of 12,500 centistokes.

EXAMPLE III

Kerosene containing 0.1% by weight di(2-ethylhexyl) 2-ethylhexylphosphonate and 0.001% by weight methyl phenyl polysiloxane fluid containing approximately 1.5 methyl groups and 0.5 phenyl group per silicon atom.

EXAMPLE IV

A gasoline composition containing 0.02% by weight tris-(3,3,5-trimethylcyclohexyl)phosphine and 0.001% by weight dimethyl polysiloxane fluid of a viscosity at 25° C. of 1000 centistokes.

EXAMPLE V

A gasoline composition containing 0.015% by weight diphenyl cresyl phosphate and 0.0003% by weight dimethyl polysiloxane fluid of a viscosity at 25° C. of 100 centistokes.

EXAMPLE VI

A cellulose-base gasket composition containing 10% by weight tricresyl phosphate and 0.15% by weight dimethyl polysiloxane fluid of a viscosity at 25° C. of 100 centistokes.

EXAMPLE VII

A cellulose-base gasket composition containing 5% by weight tributyl phosphate and 0.2% by weight dimethyl polysiloxane fluid of a viscosity at 25° C. of 60,000 centistokes.

EXAMPLE VIII

A paper composition suitable for the manufacture of gaskets containing 1% by weight dioctyl phenylphosphonate and 0.05% by weight dimethyl polysiloxane fluid of a viscosity at 25° C. of 12,500 centistokes.

EXAMPLE IX

A paper gasket containing 0.5% by weight dicresyl 2-ethylhexyl phosphate and 0.05% by weight methylethyl polysiloxane containing an average of eight silicon atoms per molecule.

EXAMPLE X

A cellulose-base gasket composition containing 20% by weight triphenyl phosphine and 1% by weight diethyl polysiloxane containing an average of about 100 silicon atoms per molecule.

EXAMPLE XI

A gasoline composition containing 0.10% by weight triphenyl phosphate and 0.001% by weight of a partially condensed methyl silicone resin having a methyl group to silicon atom ratio of 1.8.

EXAMPLE XII

A cellulose-base gasket composition containing 15% by weight tris(2-ethylhexyl) phosphate and 0.2% by weight of a partially condensed methyl polysiloxane having a methyl group to silicon atom ratio of 1.95.

EXAMPLE XIII

An automotive gasoline composition containing 0.025% weight tris(2-chloropropyl)thionophosphate and 0.0001% by weight dimethyl polysiloxane fluid having a viscosity of 500 centistokes at 25° C.

The method of treating the cellulose gasket material in accordance with the present invention can be varied extensively. It is only necessary that the silicon compound and the phosphorus compound be commingled upon the surface of the material in the proportions specified above.

As heretofore mentioned, a particularly convenient method of treating the gasket material is to incorporate the silicon compound and the phosphorus compound in the hydrocarbon liquid which is to be confined by the gasket. However, when this is not desirable, because of the necessity for excluding such compounds from the hydrocarbon, an equally effective way of preventing leakage of the hydrocarbon is to use a gasket material which has been pretreated with the silicon compound and the phosphorus compound. In such a case a liquid carrier for either or both the agents can be used or not. Either of the agents can be deposited first, followed by the other, but it is preferred that both be deposited on the surface of the material at once, for example, from a liquid carrier in which both have been dissolved, followed by removal of the carrier by distillation, evaporation, centrifugation, or any other physical means. The treatment can very conveniently and effectively be carried out at room temperature. However, if desired it may be carried out at elevated temperatures (but below the decomposition temperature of the cellulose material) to facilitate the removal of any carrier used or to facilitate the migration of the agents into the fibers of the material. Alternatively, the process can be carried out at depressed temperatures and/or under greater-than-atmospheric pressure in order that a highly volatile carrier, such as liquified petroleum gas, may be used.

Both the silicon compounds and the phosphorus compounds of the invention are very stable and relatively unreactive. Therefore, any of the common commercial solvents in which these agents are soluble or dispersible can generally be used as a liquid carrier. Examples of such suitable liquid carriers are gasoline, kerosene, amylacetate, benzene, carbon tetrachloride, ethyl ether, 2-ethylhexanol, methyl ethyl ketone, methyl isobutyl ketone, V. M. and P. naphtha, Stoddard solvent, xylene, and many others.

This application is a continuation-in-part of parent application Serial No. 450,264, filed August 16, 1954, and now abandoned.

We claim as our invention:

1. A liquid hydrocarbon fuel boiling below about 600° F. containing an anti-wicking additive combination consisting essentially of a C_1–C_7-hydrocarbyl polysiloxane having a viscosity at 25° C. of from about 0.65 to about 60,000 centistokes and being soluble to the extent of at least 1% by weight in toluene and a phosphorus compound having the formula:

$$P(X)_a(OR)_b(R)_c$$

where: X is a chalcogen atom having an atomic number from 8 to 16, inclusive; R is a monovalent radical containing no atoms other than carbon, hydrogen, and chlorine, no more than one chlorine atom, and from 1 to 10 carbon atoms; a is a whole number from 0 to 1, inclusive; b and c are whole numbers from 0 to 3, inclusive, the sum of b and c being equal to 3; and wherein the weight ratio of the phosphorus compound to the polysiloxane is from about 10:1 to about 1000:1, and the concentrations of the polysiloxane and the phosphorus compound in the liquid hydrocarbon fuel are, respectively, from about 0.00001 to about 0.05% by weight and from about 0.0001 to about 1% by weight.

2. A fuel in accordance with claim 1, wherein the polysiloxane is a di-alkyl polysiloxane.

3. A gasoline fuel containing from about .00005 to about 0.01% by weight of a di-alkyl polysiloxane having a viscosity at 25° C. of from about 10 to about 60,000 centistokes, the alkyl groups of which contain from 1 through 7 carbon atoms, and from about 0.001 to about 0.5% by weight of a phosphorus compound having the formula:

$$P(X)_a(OR)_b(R)_c$$

where: X is a chalcogen atom having an atomic number from 8 to 16, inclusive; R is a monovalent radical containing no atoms other than carbon, hydrogen, and chlorine, no more than one chlorine atom, and from 1 to 10 carbon atoms; *a* is a whole number from 0 to 1, inclusive; *b* and *c* are whole numbers from 0 to 3, inclusive, the sum of *b* and *c* being equal to 3; and wherein the weight ratio of the phosphorus compound to the polysiloxane is at least about 10:1.

4. A gasoline fuel in accordance with claim 3, wherein at least one radical of the phosphorus compound is an alkyl radical.

5. A gasoline fuel in accordance with claim 3, wherein at least one radical of the phosphorus compound is an aryl radical.

6. A gasoline fuel containing from about 0.00005 to about 0.01% by weight of a di-alkyl polysiloxane having a viscosity at 25° C. of from about 10 to about 60,000 centistokes, the alkyl groups of which contain from 1 through 7 carbon atoms, and from about 0.001 to about 0.5% by weight of a phosphorus compound having the formula:

$$P(O)_a(OR)_b(R)_c$$

where: R is a monovalent hydrocarbyl radical containing from 1 through 10 carbon atoms; *a* is a whole number 0 to 1, inclusive; *b* and *c* are whole numbers from 0 to 3, inclusive, the sum of *b* and *c* being equal to 3; and wherein the weight ratio of the phosphorus compound to the polysiloxane is at least about 10:1.

7. A gasoline fuel containing from about 0.00005 to about 0.01% by weight of a dimethyl polysiloxane having a viscosity at 25° C. of from about 10 to about 60,000 centistokes and from about 0.001 to about 0.5% by weight of a trihydrocarbyl phosphate, the weight ratio of the phosphate to the polysiloxane being at least about 10:1.

8. A gasoline fuel in accordance with claim 7, wherein the phosphate is tricresyl phosphate.

9. A gasoline fuel in accordance with claim 7, wherein the phosphate is dephenyl cresyl phosphate.

10. An automotive gasoline composition containing from about 0.0001 to about 0.0005% by weight of a dimethyl polysiloxane having a viscosity at 25° C. of about 500 centistokes and from about 0.02 to about 0.06% by weight of tricresyl phosphate.

11. A gasoline fuel in accordance with claim 3, wherein the di-alkyl polysiloxane is a dimethyl polysiloxane having a viscosity at 25° C. of from about 100 to about 30,000 centistokes.

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