

## UNITED STATES PATENT OFFICE

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## ANTIKNOCK MIXTURES

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This invention relates to a class of bromo-hydrocarbon compounds for use as scavengers with lead antiknock compounds, having a particular molecular structure and a particular vapor pressure which make them superior to scavengers heretofore known or used. These scavengers may be used alone in lead-treated fuels generally and are preferred for use in aviation fuels. According to Bartholomew Patent No. 2,398,281, issued April 9, 1946, a preferred motor fuel contains both bromo- and chloro-hydrocarbon scavengers. For this use our invention is a mixture of one or more of our bromo-hydrocarbons with one or more chloro-hydrocarbons having a particular vapor pressure.

Scavengers are materials employed with lead antiknock compounds in fuels for internal combustion engines to produce, during combustion, volatile lead compounds which are exhausted from the engine. Scavengers reduce the amount of the less volatile lead compounds which otherwise form during combustion and collect on engine parts. For satisfactory operation of an engine employing leaded gasoline, it is essential that a scavenger be used. Commercially used scavengers are ethylene dibromide and ethylene dichloride.

It has been generally believed that scavengers decompose or burn in the combustion process and release free hydrogen halides which react with the lead compounds and hence, as indicated by Midgley Patents 1,592,954 and 1,668,022, only the amount of halogen used with tetraethyllead is of importance from the standpoint of engine operation. On this basis all scavengers containing a given quantity of a specific halogen were thought to be equally efficacious. On the contrary we have found that the effectiveness of a given quantity of a halogen in engines may vary widely when introduced into the fuel in different chemical compounds, and that the several factors which determine the relative merits of different compounds are related to their molecular structure.

We have found that our bromine compounds give superior results in engines in many situations within the wide range of conditions encountered in service. In particular, our scavengers have molecular structures which, under many engine operating conditions, result in the bromine contained therein having in the engine cylinder a unit effectiveness superior to that of the scavengers heretofore used commercially. This property of effectiveness within the cylinder we call intrinsic scavenging efficiency of

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the compound. Our scavengers, in addition to high intrinsic scavenging efficiency, possess other advantages. These include an evaporation characteristic in fuel such as to give a suitable pattern of distribution in the engine relative to that of lead antiknock compounds under the range of intake manifold conditions encountered in service, high inherent stability when stored in admixture with lead antiknock compounds, and ready miscibility with lead antiknock agents. Among our scavengers are many which have only a slight tendency to reduce the antiknock effectiveness of the lead compound in the engine.

Of the scavengers known heretofore, only ethylene dibromide and ethylene dichloride have been in successful commercial use for many years. Although they have generally met the requirements of good scavengers, they are not completely satisfactory for some conditions of operation of present-day internal combustion engines, especially those engines which are used in heavy-duty service. Over a period of years the desire for higher engine output has caused a shift in engine design toward the use of intake manifolds having larger cross-sectional areas. This same objective, along with the necessity for making most efficient use of highly cracked gasoline, has lead to a decrease in the temperature of the air-fuel mixture in the intake manifold. These modifications in design not only have caused a change in the distribution pattern of the antiknock and scavengers among the individual cylinders of engines at intake manifold pressures near or above atmospheric pressure, but also have resulted in a lower temperature of the air-fuel mixture at the time its compression is started in the cylinders. We have found that ethylene dibromide and ethylene dichloride are not completely satisfactory under some conditions in meeting the requirements imposed by these changes in engine design. Although the presently used scavengers are generally satisfactory for passenger car operation, their deficiency is apparent in some engines in truck and bus service where a large percentage of the operation is at or near full-throttle, and it constitutes a serious problem in certain high-output aviation engines.

Efforts have been made to overcome this particular problem by selecting as scavengers various compounds approximating tetraethyllead in boiling point. However, the choice of a halide to obtain improvement in one property may result in degradation of other properties. For example, we have found that in storage on a commercial scale dibromochlorobutane, selected for

its low volatility, is far too unstable with tetraethyllead for commercial use. Some scavengers which have satisfactory evaporation characteristics in engines and sufficient storage stability in antiknock fluids do not have proper miscibility with tetraethyllead. Other scavengers which have been suggested are generally deficient in one or more of the above-named properties.

It is the object of our invention to provide scavengers which not only have good scavenging efficiency but also possess other properties desirable for commercial use.

Our invention is the use as scavengers of the class of bromine-substituted hydrocarbons having two to three bromine atoms and from three to eight carbon atoms inclusive, having not more than one bromine atom attached to any carbon atom, and having a vapor pressure at 50° C. of substantially 0.2 to 6 millimeters of mercury. Our invention also includes the use of these scavengers with chloro-hydrocarbons having a vapor pressure at 50° C. of substantially 0.2 to 6 millimeters of mercury.

A representative group of bromo-hydrocarbons coming within our invention, with their vapor pressures in millimeters of mercury at 50° C., is as follows:

Bromo-hydrocarbons	Approximate Vapor Pressure at 50° C.
1,3,4-Tribromopentane.....	0.2
4,5-Dibromo-1,3-dimethylbenzene.....	0.2
1,6-Dibromohexane.....	0.3
1,6-Tribromopentene-1.....	0.3
1,2,3-Tribromopentane.....	0.4
1,2,3-Tribromopentane.....	0.5
Dibromotoluenes (Mixed).....	0.6
1,2,3-Tribromopentane.....	0.7
3,4-Dibromomethylcyclohexane.....	0.7
6-Bromo-4-(bromomethyl)-heptene-1.....	0.7
1,2-Dibromocyclohexane.....	0.8
1,2,3-Tribromo-2-methylpropane.....	0.8
1,2-Dibromoheptane.....	0.8
1,2,3-Tribromopropane.....	1.0
1,2,3-Tribromopropane.....	1.0
1,2-Dibromobenzene.....	2.6
2,5-Dibromopentene-1.....	4.0
1,2-Dibromohexene-1.....	4.6
1,2-Dibromocyclopentane.....	5.5
1,3-Dibromo-2,2-dimethylpropane.....	5.5
2,3-Dibromo-2-methylpentane.....	6.3

One theory of any of the above compounds employed with tetraethyllead in gasoline gives good results in aviation engines.

The above list is merely representative and does not include all the bromo-hydrocarbons of our invention.

A representative group of chloro-hydrocarbons, to be used with our bromo-hydrocarbons, with their vapor pressure at 50° C., is as follows:

Chloro-hydrocarbons	Approximate Vapor Pressure at 50° C.
1-Chloronaphthalene.....	0.2
(5-Chloroamyl)-benzene.....	0.2
1-Chlorohendecane.....	0.5
1,8-Dichlorooctane.....	0.5
1,2,3,4-Tetrachlorocyclopentane.....	1.5
Hexachloropropylene.....	1.6
1,2,4-Trichlorobenzene.....	2.0
1,2-Dichloroheptane.....	2.4
5,6-Dichloro-3,3-dimethylhexane.....	2.8
2,4-Dichlorotoluene.....	3.2
1,2-Dichlorocyclohexane.....	4.6
1-Chlorooctane.....	5.6
5-Chloro-2,2,3-trimethylhexane.....	5.8

One-half theory of 1,2,3-tribromopropane and one theory of hexachloropropylene employed with tetraethyllead in motor fuel gives good results in vehicles on the road.

The above list is merely representative of the chloro-hydrocarbons which may be used.

The naming of bromo-hydrocarbons for use with the lead compounds in aviation fuels and of a mixture of bromo-hydrocarbons and chloro-hydrocarbons for use with the lead compounds in motor fuels merely follows present commercial trends in the use of scavengers. Such use appears to give best results.

Our scavengers in admixture with a lead antiknock compound have been added to many different base gasolines. The resulting fuels have been used in extended operation in the laboratory and on the road in numerous engines, including vehicular and high-output aviation engines and single-cylinder engines of the type commonly used for research on aviation fuels. At the end of each period of operation, examination of those engine parts which are adversely affected in the absence of a scavenger showed that our compounds were always effective scavengers and were, in light-duty operation, at least as good as those now in commercial use.

The quantity of scavenger theoretically required for reaction with the lead to form the lead halide, which quantity is two atoms of halogen per atom of lead, is called one theory of halogen. Present commercial practice is to use one theory of bromine in aviation fuels, while for motor fuels one-half theory of bromine is used with one theory of chlorine. In the engine operations described below, the scavengers were used in amounts providing the number of theories of halogen employed in commercial practice.

On the road, our scavengers were employed in heavy-duty operation of a fleet of commercial trucks. 1,2,3-tribromopropane, in combination with hexachloropropylene, was blended with tetraethyllead and incorporated in a gasoline which was used in part of the fleet. A treated fuel consisting of the same base gasoline containing tetraethyllead and a mixture of ethylene dibromide and ethylene dichloride as the scavenger was used in the remainder of the fleet. Since the conditions were identical except for the scavenger composition, any difference in lead deposits and corrosion of the engines was attributable to the differences in the scavengers. Each of the trucks was operated on a twenty-four hour per day basis while carrying a gross load of about 32,000 pounds. The exhaust valve life, based on miles to the first two valve failures in each engine, on the average was 30% greater for the trucks operating on the fuel containing our scavengers than on the fuel containing the commercial mixture of ethylene dibromide and ethylene dichloride. In heavy-duty operation of this type, the durability of exhaust valves is a critical factor, and improvements of the above magnitude are of great importance to the owners of trucks and busses, because of decreased expense of maintenance and greater availability of the vehicles for operation on the road.

Our scavengers have also been used with greatly improved efficiency in commercial aircraft engines operated under conditions comparable to those encountered in flight. For example, high-output liquid-cooled aviation engines operated with three different scavengers, namely ethylene dibromide, 1,2,3-tribromopropane and mixed dibromotoluenes, the last two being scavengers of our invention. Each operation was 120 hours in duration on a fuel containing 4.6 milliliters of tetraethyllead per U. S. gallon and 1.0 theory of one of the above-named bromo-hydrocarbon scavengers. Inspection of the valves and spark plugs at the end of each period of operation

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showed that strikingly superior results were obtained with our scavengers. When ethylene dibromide was used, exhaust valves were severely burned. When our scavengers were used, there was no valve burning.

We believe that these improved results are due in part to superior intrinsic scavenging efficiency and in part to a pattern of distribution to the different cylinders in the engine which is closer to that of tetraethyllead. This belief is substantiated by results from two other kinds of engines. One type of engine provided a comparison of the intrinsic scavenging efficiency and the other a comparison of the distribution characteristics of our scavengers with those of scavengers heretofore known, and particularly with those of scavengers heretofore used commercially.

In single-cylinder laboratory engines commonly used for research on aviation fuels and spark plugs, where there can be no distribution problem, a comparison was made of the dry weight of the combustion chamber deposit after extended operation with one theory of different bromine scavengers. This deposit weight may be taken as one measure of intrinsic scavenging efficiency. The following table is illustrative of the results which may be obtained:

Scavenger	Percent Deposit Relative to Ethylene Dibromide as 100%
1, 3-Dibromo-2, 2-dimethylpropane.....	91
1, 6-Dibromohexane.....	78
1, 2-Dibromocyclohexane.....	84
1, 2, 3-Tribromopropane.....	79
1, 2, 3-Tribromobutane.....	83
1, 2, 3-Tribromo-2-methylpropane.....	80

It is significant and entirely unexpected that many of the bromo-hydrocarbons of our invention have an intrinsic scavenging efficiency which is superior to that of ethylene dibromide. A further significant finding is that other bromo-hydrocarbons which, because of similarity of molecular structure, might be expected to behave like our compounds in respect to intrinsic scavenging efficiency, but which have vapor pressures falling outside our range, are far less efficient. For instance, the use of 1-bromocetane, which has a vapor pressure at 50° C. of 0.005 millimeter of mercury, gave even a greater amount of deposit than did ethylene dibromide.

We believe that the superiority of our scavengers in truck and aviation engine operation is accounted for not only by higher intrinsic scavenging efficiency but also by improved evaporation characteristics. Sometimes there is pronounced maldistribution of tetraethyllead to the different cylinders in certain types of engines. While this maldistribution is more pronounced in aircraft engines, it is also a problem in some passenger and heavy-duty motor vehicles under certain conditions of operation. When distribution is not a factor, it is known that poorer engine durability is obtained when the fuel used contains either too little or too much scavenger for the tetraethyllead used. Poor engine durability is obtained if one cylinder receives a scavenger in excessive or in deficient quantities relative to the tetraethyllead present. Either condition may cause premature failure of the spark plug and the exhaust valve for that cylinder, and this may be accompanied by excessive lead deposits when there is a deficiency of scavenger.

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When a mixture of fuel and air flows from the carburetor into the manifold and partial vaporization of the fuel occurs, the proportions of the fuel in the vapor and liquid state during passage through the intake manifold vary widely with engines, fuels, and operating conditions, such as engine speed, ambient air temperature and other factors. In the operation of a currently produced automotive engine with various typical motor gasolines, we have found as much as 5% of the fuel present in the form of liquid flowing along the walls of the manifold, the remaining portion of the fuel being present as vapor and entrained liquid. The concentration of tetraethyllead in the liquid portion of the fuel flowing along the manifold walls is generally far higher than that in the original fuel, so that a considerable part of the total quantity of tetraethyllead input may remain in the relatively small amount of liquid on the manifold walls. If this liquid portion of the fuel does not distribute evenly, some cylinders receive widely disproportionate amounts of tetraethyllead. In certain types of operations we have found variations in tetraethyllead input to motor vehicle cylinders of as much as 50%. Much wider variations have been found in aircraft engines, the tetraethyllead input to individual cylinders varying from 45% to 400% of the average amount.

The pattern of distribution of the scavenger to the engine cylinders may be entirely different from that of the tetraethyllead. We have found by measurements that even when the tetraethyllead is present in a high concentration in the liquid flowing along the manifold, the scavengers of our invention follow the lead more closely than the scavengers presently used.

To illustrate the relative quantities of various bromo-hydrocarbon scavengers present in the liquid portion of the fuel flowing along the wall of the manifold, a currently-produced eight-cylinder, valve-in-head automotive engine was used in which the liquid flowing along the walls of the manifold branches for each pair of cylinders was collected. This liquid was analyzed to determine its tetraethyllead and scavenger content. In all cases the same base gasoline containing three milliliters of tetraethyllead per gallon with one theory of bromine was used, and each operation was carried out under as nearly identical conditions as possible. The following tables give the theories of bromine relative to the lead present in the liquid for a representative group of our scavengers and, for comparison, the same information for several scavengers which do not lie within our invention.

	Vapor Pressure (mm. of Mercury at 50° C.)	Theories of Bromine for the Lead in Liquid Collected from Manifold
<i>Scavengers Within Our Invention</i>		
1, 6-Dibromohexane.....	0.3	1.5
Dibromotoluenes (Mixed).....	0.5	1.8
1, 2, 3-Tribromobutane.....	0.7	1.1
1, 2-Dibromocyclohexane.....	0.8	1.1
1, 2, 3-Tribromo-2-methylpropane.....	0.8	1.2
1, 2, 3-Tribromopropane.....	1.0	0.8
1, 2-Dibromohexene-1.....	4.0	0.7
1, 3-Dibromo-2, 2-dimethylpropane.....	5.5	0.6
<i>Scavengers not Within Our Invention</i>		
1-Bromocetane.....	0.005	4.1
1, 2, 3, 4-Tetrabromocyclopentane.....	0.03	3.8
1, 3-Dibromopropane.....	11.0	0.1
Ethylene dibromide.....	40.2	0.05

Although data of this type depend to a large degree on the base gasoline and conditions of operation used, they are illustrative of the trends produced by differences in vapor pressure and molecular structure, and they serve to emphasize the advantage of our scavengers. These data are illustrative of the improvement in distribution relative to the lead antiknock compound which can occur with our scavengers. In the preceding table, scavengers within our invention vary in concentration relative to the lead over a relatively narrow range, whereas those scavengers which are not within our invention depart more widely from the one theory of bromine supplied in the input fuel.

The distribution of the scavenger and of the tetraethyllead among the cylinders of an engine we call the pattern of distribution of each. We have found that the patterns of distribution of our bromine scavengers are much closer to that of the tetraethyllead than the patterns of other known bromine scavengers.

We use chloro-hydrocarbons having a vapor pressure comparable to that of our bromo-hydrocarbons to obtain a comparable pattern of distribution. We find that these chloro-compounds are generally more stable than the corresponding bromo-compounds, and we believe that molecular structure is not as important a factor in the selection of a chlorine scavenger.

Determinations were also made of the distribution of tetraethyllead and scavengers to the individual cylinders of a multi-cylinder engine. One-half theory of ethylene dibromide plus one theory of ethylene dichloride was compared with one-half theory of one of our bromine scavengers, 1,2,3-tribromopropane, plus one theory of one of our chlorine scavengers, hexachloropropylene. The maximum variation in theories of bromine from the average among the cylinders was 22% and in theories of chlorine 15% for the mixture containing ethylene dibromide and ethylene dichloride. For the mixture containing our scavengers the maximum variation in theories of bromine was only 8% and in the theories of chlorine only 6%. The variation among the cylinders in the ratios of our scavengers to the lead may be greater or less than in the above illustration, depending on the engine, operating conditions of the engine and the specific scavengers used. Under a wide range of operating conditions our scavengers give improved results.

The improvement in pattern of distribution of our scavengers relative to the pattern of distribution of the lead antiknock, as illustrated here, supports the belief that better relative distribution accounts in part for improved engine durability associated with the use of our scavengers in truck fleet and high-output aviation engine operations in which troubles attributable to distribution have been encountered.

We have found that the boiling point of a scavenger is not a reliable index of its evaporation relative to that of tetraethyllead in the engine manifold. For example, 1,2,3-tribromopropane, having a boiling point 20° C. higher than that of tetraethyllead, would normally be expected to evaporate less readily and to cause the concentration of bromine to be more than one theory in the liquid which flows along the walls of the manifold. In actual engine operation, however, the liquid flowing along the walls of the manifold contained substantially less than one theory of bromine.

Since the ratios of the vapor pressures of the scavengers to that of tetraethyllead vary consid-

erably with temperature, it is desirable to select a reference temperature which is suitably related to the conditions of actual evaporation in the manifold, rather than to choose an arbitrary point of reference such as room temperature. We have found that a reference temperature of 50° C. satisfies this requirement and that the vapor pressures of halogen compounds at this temperature serve as a general index of their distribution in engines. Under the worst conditions in respect to distribution of tetraethyllead in the engine, best results may be expected from the use of our scavengers whose vapor pressure at 50° C. lies between 0.5 and 2 millimeters of mercury. The vapor pressure of tetraethyllead at 50° C. is 2.1 millimeters of mercury.

In addition to the foregoing, there are other properties which scavengers should possess for commercial acceptability. The storage stability of antiknock fluids containing scavengers is highly important to the shipping and storing of such fluids, either alone or in gasolines. Under normal storage or shipping conditions, antiknock fluids containing lead compounds may decompose to a slight extent even when the most stable scavengers are incorporated. When lead antiknock fluids or fuels containing lead antiknock fluids are to be stored for periods of several years, especially at elevated temperatures, it is desirable that the stability of the antiknock fluids be high.

When the antiknock fluid decomposes, lead salts are either precipitated or remain in solution in the fluid, from which they may precipitate when the fluid is blended with gasoline. Decomposition is accompanied by the evolution of gas which causes pressure to be built up in the containing drum or tank car. In cases of severe decomposition, due to marked instability of the antiknock fluid, the pressure may rise to a point sufficiently high to cause leakage or rupture of the container. Decomposition destroys some of the antiknock properties of the lead compound in the fluid and consequently renders uncertain the antiknock effect to be expected from the addition of a given volume of antiknock fluid to gasoline.

If desired, the stability of the antiknock fluid mixture may be temporarily improved by the addition of certain antioxidants, such as the alkyl-substituted phenol of Walters' Patent No. 2,361,377. In contrast to the good stability of our scavengers, many of the bromo-hydrocarbons whose molecular structure does not conform to our specification, such as 1,1,2,2-tetrabromoethane, are so unstable with tetraethyllead, even with the addition of antioxidants, as to be unsatisfactory for commercial use as scavengers.

Some halogen compounds which might be considered for use as scavengers are unsatisfactory because they react in the engine with the lead antiknock compound to reduce the antiknock effectiveness of a given concentration of the lead antiknock compound. Our scavengers vary in this respect. The number of scavengers from which to make a selection is large enough so that compounds can be selected which do not decrease antiknock effectiveness materially.

A desirable property for a commercial scavenger is complete miscibility with the lead antiknock compounds, down to low temperatures, so that the mixture will not separate when stored and handled in cold weather. If desired, the minimum temperature of complete miscibility may be lowered, by the addition of a mutual solvent. The same effect may also be achieved by using, instead

of a single scavenger, a mixture of two or more scavengers.

Our scavengers may be used with lead compounds other than tetraethyllead, such as tetrapropyllead, dimethyldiethyllead, and methyltriethyllead. Where a mixture of lead antiknock compounds is employed, the scavenger may be one of our bromo-hydrocarbons or a mixture of two or more of them. It is customary to make a blend of the lead antiknock compound and the scavenger and then to add this mixture to a gasoline. However, the scavenger and antiknock compound may be added separately to the fuel.

The properties of our scavengers vary sufficiently to permit a selection for any specific conditions of use. For example, where storage stability is of prime importance the bromo-aromatic scavengers of our invention may be selected, while if high intrinsic scavenging ability is most desired our saturated bromo-aliphatic hydrocarbon scavengers are preferred. Where distribution in the engine relative to that of tetraethyllead is the principal problem, our scavengers having a vapor pressure between 0.5 and 2 millimeters of mercury at 50° C. are preferred.

For purposes of comparison, the proportions of scavengers used in the above examples have been the same, i. e., one theory of bromo-hydrocarbon for the lead compounds in aviation gasolines, and a mixture of one-half theory of a bromo-hydrocarbon and one theory of a chloro-hydrocarbon for the lead compounds in motor fuels. The use of our scavengers is not critical, and therefore is not so limited. For aviation fuels, best results have been obtained with proportions varying from 0.8 theory to 1.5 theories, and a wider variation may be used. For motor fuels we recommend the proportions of scavengers set forth in Bartholomew Patent No. 2,398,281.

We claim:

1. An antiknock composition consisting essentially of a lead antiknock compound and a scavenger in an amount sufficient to reduce the deposition of lead in the engine by forming volatile lead compounds, a principal active scavenging ingredient of which is a bromo-hydrocarbon having two to three bromine atoms and from three to eight carbon atoms inclusive, having not more than one bromine atom attached to any carbon atom, and having a vapor pressure at 50° C. of substantially 0.2 to 6 millimeters of mercury.

2. An antiknock composition consisting essentially of tetraethyllead and a scavenger in an amount sufficient to reduce the deposition of lead in the engine by forming volatile lead compounds, a principal active scavenging ingredient of which is a bromohydrocarbon having two to three bromine atoms and from three to eight carbon atoms inclusive, having not more than one bromine atom attached to any carbon atom, and having a vapor pressure at 50° C. of substantially 0.2 to 6 millimeters of mercury.

3. An antiknock composition consisting essentially of a lead antiknock compound and a scavenger in an amount sufficient to reduce the deposition of lead in the engine by forming volatile lead compounds, a principal active scavenging ingredient of which is a bromo-hydrocarbon having two to three bromine atoms and from three to eight carbon atoms inclusive, having not more than one bromine atom attached to any carbon atom, and having a vapor pressure at 50° C. of substantially 0.5 to 2 millimeters of mercury.

4. An antiknock composition consisting essen-

tially of a lead antiknock compound and approximately one-half theory of a bromo-hydrocarbon scavenger having two to three bromine atoms and from three to eight carbon atoms inclusive, having not more than one bromine atom attached to any carbon atom, and having a vapor pressure at 50° C. of substantially 0.5 to 2 millimeters of mercury, in admixture with approximately one theory of a chloro-hydrocarbon having a vapor pressure at 50° C. of substantially 0.2 to 6 millimeters of mercury.

5. A composition of matter as defined in claim 1 wherein the bromo-hydrocarbon is a saturated bromo-aliphatic hydrocarbon.

6. A composition of matter as defined in claim 1 wherein the bromo-hydrocarbon is a bromo-cycloaliphatic hydrocarbon.

7. A composition of matter as defined in claim 1 wherein the bromo-hydrocarbon is a bromo-aromatic hydrocarbon.

8. An antiknock composition consisting essentially of a lead antiknock compound and a scavenger in an amount sufficient to reduce the deposition of lead in the engine by forming volatile lead compounds, a principal active scavenger ingredient of which is dibromobenzene.

9. An antiknock composition consisting essentially of a lead antiknock compound and a mixture of scavengers each of which is present in an amount sufficient to reduce the deposition of lead in the engine by forming volatile lead compounds, the principal active scavenging ingredients of which are a bromo-hydrocarbon having two to three bromine atoms and from three to eight carbon atoms inclusive, having not more than one bromine atom attached to any carbon atom, and having a vapor pressure at 50° C. of substantially 0.2 to 6 millimeters of mercury, and a chloro-hydrocarbon having a vapor pressure at 50° C. of substantially 0.2 to 6 millimeters of mercury.

10. An antiknock composition consisting essentially of a lead antiknock compound and a mixture of scavengers each of which is present in an amount sufficient to reduce the deposition of lead in the engine by forming volatile lead compounds, the principal active scavenging ingredients of which are 1, 2, 4-trichlorobenzene and a bromo-hydrocarbon having two to three bromine atoms and from three to eight carbon atoms inclusive, having not more than one bromine atom attached to any carbon atom, and having a vapor pressure at 50° C. of substantially 0.2 to 6 millimeters of mercury.

11. An antiknock composition consisting essentially of a lead antiknock compound and a scavenger in an amount sufficient to reduce the deposition of lead in the engine by forming volatile lead compounds, a principal active scavenging ingredient of which is dibromotoluene.

12. An antiknock composition consisting essentially of a lead antiknock compound and a mixture of scavengers each of which is present in an amount sufficient to reduce the deposition of lead in the engine by forming volatile lead compounds, the principal active scavenging ingredients of which are dibromotoluene, and a chloro-hydrocarbon having a vapor pressure at 50° C. of substantially 0.2 to 6 millimeters of mercury.

13. An antiknock composition consisting essentially of a lead antiknock compound and a mixture of scavengers each of which is present in an amount sufficient to reduce the deposition of lead in the engine by forming volatile lead

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compounds, the principal active scavenging ingredients of which are dibromotoluene and 1, 2, 4-trichlorobenzene.

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