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## ANTIKNOCK MIXTURES

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This invention relates to a particular group of chlorohydrocarbons, for use as scavengers with lead antiknock compounds. According to Bartholomew Patent No. 2,398,281, issued April 9, 1946, a preferred motor fuel contains both chloro- and bromo-hydrocarbon scavengers. Therefore it is preferable to mix one of our chloro-hydrocarbons with one or more bromohydrocarbons.

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 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 generally been believed that in an engine cylinder all scavengers containing a given quantity of a specific halogen are equally efficacious. This property of unit effectiveness within the cylinder we call intrinsic scavenging efficiency, and we have found that it varies for different halogen compounds. Other desirable properties of scavengers include stability when stored in admixture with lead antiknock compounds, miscibility with lead antiknock compounds, freedom from reduction in effectiveness of lead antiknock compounds, and volatility giving 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.

It is an object of our invention to provide a new class of scavengers having not only good intrinsic scavenging efficiency but also other properties desirable for commercial use.

Our invention is directed to the use as scavengers of aromatic hydrocarbons of the benzene series containing 6 to 8 carbon atoms, having 2 to 3 chlorine atoms attached directly to the benzene ring, and having a vapor pressure at 50° C. within the range of about 0.2 to 6 millimeters of mercury. Preferably our chlorohydrocarbons should have a vapor pressure at 50° C. within the range of 0.5 to 2.0. The vapor pressure of tetraethyllead at 50° C. is about 2.1 millimeters of mercury.

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A representative group of our chlorohydrocarbons with their vapor pressures at 50° C. is as follows:

| Chlorohydrocarbons | Approximate Vapor Pressure at 50° C. |
|---|---|
| 2,3-dichloro-1,4-dimethylbenzene | 0.5 |
| Dichloroxylenes (mixed) | 0.6 |
| 3,4-dichlorocumene | 0.6 |
| 2,3,4-trichlorotoluene | 0.6 |
| 3,4,6-trichloro-1,2-dimethylbenzene | 0.7 |
| 1,2,3-trichlorobenzene | 1.2 |
| 1,2,4-trichlorobenzene | 2.0 |
| 1,3,5-trichlorobenzene | 2.0 |
| 2,4-dichlorotoluene | 3.2 |

It is to be understood that mixtures of these compounds may be used, and this is frequently more economical since manufacturing processes may produce mixtures, and the expense of isolating one compound from the others may be avoided.

Present commercial practice is to mix a chlorohydrocarbon and a bromohydrocarbon for use with the lead compounds in motor fuels. Therefore to obtain the best results, one of our scavengers is used with one or more bromine scavengers.

Our scavengers and various bromine scavengers in admixture with a lead antiknock compound have been added to different base gasolines, and used in internal combustion engines. 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 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 practice for motor fuels is to use one-half theory of bromine plus one theory of chlorine.

One theory of 1,2,4-trichlorobenzene or others of our chlorohydrocarbons and one-half theory of monobromoxylene (mixed) or other bromohydrocarbons employed with tetraethyllead in motor fuel gives good results in vehicles on the road.

To illustrate the scavenging efficiency of our scavengers, 1 theory of 1,2,4-trichlorobenzene in

admixture with ½ theory of ethylene dibromide was blended with tetraethyllead, incorporated in gasoline, and used in an internal combustion engine. Visual inspection and measurements of engine deposits indicated that good scavenging efficiency was obtained.

In addition to good intrinsic scavenging efficiency, our compounds possess the other desirable properties mentioned above. For example, for use in certain engines our scavengers have evaporation characteristics under conditions existing in the intake manifold sufficiently close to those of tetraethyllead to ensure good distribution of the scavenger between the different cylinders of the engine. This avoids the harmful effects caused either by an excess or a deficiency in the theories of halogen for the lead in any cylinder. On the other hand, ethylene dibromide and ethylene dichloride have vapor pressures so much higher than that of tetraethyllead that they tend to give relatively poor patterns of distribution.

The storage stability of antiknock fluids containing scavengers is highly important in the shipping and storage of such fluids, either alone or in gasolines. 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 evolution of gas which causes pressure to be built up in the containing drum or tank car. The chlorohydrocarbon scavengers of our invention are satisfactory in respect to storage stability and our chloroaromatics are generally superior to ethylene dibromide and ethylene dichloride.

Miscibility of scavengers with lead antiknock compounds and freedom from reduction in the effectiveness of lead antiknock compounds are important commercially. Our scavengers generally are satisfactory in these respects.

Our scavengers may be used with lead compounds other than tetraethyllead, such as tetrapropyllead, dimethyldiethyllead, and methyltriethyllead. 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 the antiknock compound may be added separately to the fuel.

The concentration of our scavengers is not critical and therefore is not so limited. In general, 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, the principal active ingredient of which is an aromatic hydrocarbon of the benzene series, containing 6 to 8 carbon atoms, having 2 to 3 chlorine atoms attached directly to the benzene ring, and having a vapor pressure at 50° C. of between about 0.2 to 6 millimeters of mercury.



2. 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, the principal active ingredient of which is trichlorobenzene.

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, the principal active ingredient of which is trichlorotoluene.

4. An antiknock composition consisting essentially of tetraethyllead 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 ethylene dibromide and an aromatic hydrocarbon of the benzene series, containing 6 to 8 carbon atoms, having 2 to 3 chlorine atoms attached directly to the benzene ring, and having a vapor pressure at 50° C. of between about 0.2 to 6 millimeters of mercury.

5. An antiknock composition consisting essentially of tetraethyllead 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 ethylene dibromide and trichlorobenzene.

6. An antiknock composition consisting essentially of tetraethyllead 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 ethylene dibromide and trichlorotoluene.

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