United States Patent Office

2,722,477

Patented Nov. 1, 1955

2,722,477

STABILIZED FUEL ANTIKNOCK

Eugene F. Hill, Detroit, Mich., assignor to Ethyl Corporation, New York, N. Y., a corporation of Delaware

No Drawing. Application October 20, 1951, Serial No. 252,399

9 Claims. (Cl. 44—69)

This invention relates to the stabilization of antiknock compounds and to the stabilization of motor fuels containing such antiknocks.

The fuel requirements of the modern internal combustion spark ignition engine are such that each ingredient of such fuels must maintain the quality and original characteristics present when the fuels were blended. In order to provide the high octane rating required by high compression internal combustion engines, it is customary to include in the fuel an antiknock additive. Of such additives the most widely used is tetraethyllead. The amount of tetraethyllead employed in hydrocarbon fuels varies with the type of fuel and with the type of engine in which it is to be used. For example for use in automotive engines it is customary to employ between about 0.5 and 3 cc. of tetraethyllead per gallon of fuel, depending upon the lead susceptibility and quality of the base stock. On the other hand for use in aircraft engines the amount of tetraethyllead employed is ordinarily between the limits of about 3 and 6 cc. per gallon of fuel. Under unusual circumstances each of these limits can be varied although the above figures are commonplace under present fuel and engine conditions. Along with tetraethyllead a scavenging agent is employed which upon combustion of the fuel combines with the products of combustion of the tetraethyllead to place the lead in a condition wherein it can be discharged from the engine without causing unnecessary build up of solid deposits on the internal surfaces of the combustion chamber, the spark plugs or the inlet or exhaust valves. The most common practice is to employ an organic halogen compound as a scavenger. The most common of the scavenging agents comprise ethylene dichloride and ethylene dibromide. However, recently a wide variety of halogen compounds having particularly desirable properties have been developed. Among such scavenging agents are dibromotoluene, trichlorobenzene, bromoxylene and the like.

Although by ordinary chemical standards the tetraethyllead and the halogen scavenging agents can be considered as stable materials, under certain conditions, a small amount of decomposition occurs. In spite of the slowness and limited extent of such decomposition, this decomposition can become important and in many instances critical to the satisfactory operation of an internal combustion engine. Although the mechanism of such decomposition is not clearly understood, the final products of such degradation have been established as being caused by the interaction of the halogen scavenging agents and some primary decomposition product of the tetraethyllead. The evidence of such decomposition is ordinarily a haze or even a sludge precipitate, either in the concentrated antiknock fluid or in the finished gasoline. Regardless of the mechanism involved in this decomposition the fuel becomes deteriorate thereby. The net result, aside from mechanical difficulties caused by the precipitated solids, such as plugged filters and fuel lines and deposition in carburetor jets and on inlet manifolds, the fuel loses octane rating and is unable to perform as specified in the engine.

It is therefore an object of my invention to provide means for preventing the decomposition of tetraethyllead antiknock compounds. It is a further object to provide a concentrated antiknock material which is stable on storage, manufacture or handling and to further provide fuels for internal combustion engines containing tetraethyllead antiknock compounds which are likewise stable on storage, manufacture, handling or use. Still further objects will be apparent from the description of my invention hereinafter.

The above and other objetcs of my invention can be accomplished by providing tetraethyllead antiknock mixtures containing a minor proportion of 2-aminodiphenylamine. These objects can be achieved either by combining the 2-aminodiphenylamine with the tetraethyllead in the presence or absence of halogen scavengers or by including said 2-aminodiphenylamine in motor fuel containing tetraethyllead.

It is known in general that certain aromatic amines are capable of preventing the degradation of hydrocarbon fuels in the presence of oxygen. Such degradation ordinarily is evidenced by gum formation in the fuel or gum deposition on engines in which such degraded fuels have been employed. In general this problem with regard to the fuel is distinct from the problem described heretofore of stabilizing the tetraethyllead antiknock compound. In this latter problem the role of oxygen is little understood, and its significance has not been established. Typical conditions under which excessive decomposition of antiknock compounds can occur include drum storage of the concentrated antiknock fluid under conditions of constant high temperature, as encountered in desert storage, or under conditions of cycling high and low temperatures as frequently encountered in transportation of such fluids throughout the world. Likewise gasolines or other motor fuels containing such antiknock compounds are frequently subjected to similar conditions with resultant deterioration of the antiknock component.

This problem has been recognized for some time and a number of suggestions have been made for preventing such decomposition. However none of these suggestions has been completely satisfactory. To demonstrate the exceptional degree of stability imparted to antiknock compounds and the extremely minor quantities of my stabilizer which it is required to employ I have performed the following determinations.

Example I

To a fuel consisting essentially of isooctane, which is normally resistant to deterioration, was added 4.6 ml. of tetraethyllead per gallon. The tetraethyllead was previously admixed with one theory of ethylene dibromide—that is it contained the amount of ethylene dibromide which is required to react under combustion conditions with the tetraethyllead to convert all the tetraethyllead to lead bromide. One hundred milliliters of this fuel was placed in a stainless steel bomb which was sealed and heated to a temperature of 100° C. for a period of 16 hours. At the end of this time the bomb was cooled to a temperature of about 25° C., opened and the contents removed to a glass bottle. It was observed that the fuel which was initially clear and transparent contained a heavy precipitate or sludge containing lead and bromine.

The above operations were repeated but before subjecting the fuel to the high temperature varying amounts of 2-aminodiphenylamine were added to each of several samples of the above fuel. After a series of determinations, the minimum quantity of the additive was established which would permit the fuel to be heated under these conditions for this period of time without the formation of a

haze or any visible precipitate. From these results it was established that the 2-aminodiphenylamine, the stabilizer of my invention, was effective under these conditions at the extremely small concentration of 0.05 mg. per 100 ml. of fuel.

As an alternative to the addition of the stabilizing compounds of my invention to the hydrocarbon fuel containing the lead antiknock compound I can achieve equally good protection by introducing the stabilizer to the concentrated antiknock fluid. This, of course, is the preferred method of practicing my invention under conditions wherein the fluid is subjected to adverse storage or handling conditions. For example I can add 2-aminodiphenylamine in amounts between 0.01 and 3.00 weight per cent of the tetraethyllead present in an antiknock fluid containing ethylene dibromide as the principal scavenger, a mixture of the ethylene dibromide and ethylene dichloride, or other scavengers such as for example dibromotoluene, trichlorobenzene and bromoxylene. The following examples will serve to illustrate this embodiment of my invention.

Example II

To an antiknock compound comprising 100 parts of tetraethyllead with ½ theory of ethylene dibromide and 1 theory of ethylene dichloride, wherein the term "theory" has the same meaning as above, was added 0.1 part by weight of 2-aminodiphenylamine. The resulitng fluid was maintained at a temperature of 104° F. for a period of one month. At the end of this time the fluid was clear—that is it contained no precipitated solids or haze. A determination of the extent of decomposition of the tetraethyllead was made by extracting the fluid with an aqueous ammonia solution and determining the amount of lead so extracted. Thus was determined the so-called "ammonia-soluble lead," a direct measure of the extent of decomposition of the tetraethyllead. The fresh fluid contained 0.25 gram of ammonia-soluble lead per 100 ml. of tetraethyllead in the fluid. After storage as above in the presence of 0.1 weight per cent 2-aminodiphenylamine the ammonia-soluble lead was only 0.45 gram per 100 ml. of tetraethyllead, or an increase of only 80 per cent. In contrast, this same antiknock compound was stored as above without the prior addition of 2-aminodiphenylamine and developed, after one month, 2.18 grams of ammonia-soluble lead, per 100 ml. of the tetraethyllead, an increase of 770 per cent.

Example III

An antiknock compound designed for use in aircraft engines consisting of tetraethyllead and one theory of ethylene dibromide, and a small quantity of an oil soluble blue dye and to which had been added 0.1 part by weight of 2-aminodiphenylamine per 100 parts by weight of tetraethyllead in the fluid was stored at a temperature of 104° F. for one month. At the end of this period the fluid was observed and found to contain no precipitate or haze and when viewed with a strong light, the fluid possessed the original clear blue color. Determination of the ammonia-soluble lead as in Example II showed only 0.24 gram of lead per 100 ml. of tetraethyllead present, compared to 0.15 gram per 100 ml. in the original fluid.

In a duplicate determination wherein 4-aminodiphenylamine was employed in place of the 2-aminodiphenylamine at a concentration of 1 part by weight per 100 parts of tetraethyllead in the fluid of Example III, the ammonia-soluble lead after one month's storage at a temperature of 104° F. was 1.74 grams per 100 ml. of tetraethyllead. Thus, even at 10 times the concentration a seven-fold increase in the amount of amomnia-soluble lead occurred in contrast to 2-aminodiphenylamine. Thus, my stabilizer was over 70 times as effective on a weight basis. In a control determination, the above fluid, in the absence of a stabilizing additive developed 2.75 grams of ammonia-soluble lead per 100 ml. of tetraethyllead after storage for one month at 104° F.

The 2-aminodiphenylamine stabilizer of my invention can be incorporated into the fuel along with the antiknock compound as described above. However, if it is desired to add the stabilizer to the finished high octane lead-containing gasoline, I have found that a number of methods of introducing the stabilizer are effective. For example, the 2-aminodiphenylamine can be directly added to the fuel as it is recovered during the refinery operation and prior to the addition of the tetraethyllead antiknock compound, or it can be added to the finished fuel after blending with the antiknock compound. One of my preferred methods of introducing the 2-aminodiphenylamine which does not affect the ultimate efficiency of stabilization of the tetraethyllead is in the form of a liquid formulation wherein the amine is predissolved in a ketone such as acetone, methylethyl ketone, methyl isopropyl ketone, diisopropyl ketone, diisobutyl ketone and the like wherein the 2-aminodiphenylamine is present in an amount between about 10 and 50 weight per cent of such finished liquid formulation. Although it is not essential that the amine be so formulated prior to admixture to the fuel or the antiknock compound, I have found that by so doing the blending operation is simplified and uniformity of blending is assured.

The amount of 2-aminodiphenylamine which I employ to protect the tetraethyllead antiknock additive is not critical from the standpoint that the employment of more than the minimum amount required does not affect the stability of the resulting mixture. However, a practical upper limit is imposed on the concentration of the 2-aminodiphenylamine by the requirements mentioned previously of the modern high compression engine. This is one particular advantage of 2-aminodiphenylamine, in that it can be employed where other stabilizing compounds would be required in too high concentrations to permit use in such engines. The minimum amount of 2-aminodiphenylamine depends to a large extent upon the concentration of tetraethyllead in the gasoline and upon the gasoline type. For example in a highly stable gasoline such as the average aviation fuel and in the presence of about 4.0 ml. of tetraethyllead per gallon of fuel, I prefer to employ my 2-aminodiphenylamine in an amount of between about .02 and 0.2 mg. per 100 ml. of fuel. Furthermore, if the gasoline is of the unstable type the amount of 2-aminodiphenylamine will depend somewhat upon this instability. If the unstable gasoline has not previously been stabilized with a gasoline antioxidant, a larger amount of the 2-aminodiphenylamine will be required. However, in such cases the amount of 2-aminodiphenylamine will be far less than the total quantity of a gasoline antioxidant plus 2-aminodiphenylamine which would be required. Thus when 2-aminodiphenylamine alone is used in an unstable gasoline containing tetraethyllead a far smaller amount of total stabilizing ingredients can be employed than has heretofore been possible with resulting improvement in the operation of the internal combustion engine using such fuel.

The effectiveness of 2-aminodiphenylamine as a tetraethyllead stabilizer is largely independent of the fuel type. Thus I have obtained equally good results when employing 2-aminodiphenylamine to stabilize tetraethyllead in such diverse fuels as straight run paraffins, thermally and catalytically cracked high octane gasoline, highly aromatic aviation fuels and alkylate fractions suitable for use as such or further blending. In general, when the fuel is more unstable than the tetraethyllead, my stabilizer can effectively stabilize both the gasoline and the tetraethyllead when present at high enough concentrations, or a gasoline antioxidant can be employed to protect the hydrocarbon fuel and the 2-aminodiphenylamine can be employed to protect the tetraethyllead antiknock ingredient.

Incorporated directly in the antiknock fluid I can employ as little as 0.01 weight per cent of 2-aminodiphenylamine based on the tetraethyllead content of such fluid or as much as 3.0 weight per cent. My preferred limits,

however, are between about 0.05 and 1.0 weight per cent.

Several methods of manufacturing 2-aminodiphenylamine are satisfactory. One method which I prefer comprises the reduction of 2-nitrodiphenylamine with iron filings and hydrochloric acid. Other methods of reduction are similarly effective, for example catalytic hydrogenation. The 2-nitrodiphenylamine is readily prepared by nitration of diphenylamine.

Having thus described typical methods of employing the 2-aminodiphenylamine of my invention as a stabilizer for tetraethyllead, for tetraethyllead-containing antiknock compounds and for tetraethyllead-containing high octane hydrocarbon fuels, I do not intend that my invention be limited except by the appended claims.

I claim:

1. An antiknock composition wherein the principal antiknock ingredient is tetraethyllead and, as a stabilizer therefor, 2-aminodiphenylamine in amount between about .05 and 1.0 part by weight per 100 parts of said tetraethyllead antiknock ingredient.

2. A hydrocarbon fuel composition containing tetraethyllead as a principal antiknock ingredient in amount up to about 6 cc. per gallon of fuel and 2-aminodiphenylamine present in amount up to about 3.0 weight per cent of said tetraethyllead.

3. The method of preventing instability of tetraethyllead antiknock compounds which comprises incorporating therein 2-aminodiphenylamine in an amount between about 0.05 and 1.0 part by weight per 100 parts of said tetraethyllead antiknock ingredient.

4. The antiknock composition of claim 1 having incorporated therein an aliphatic ketone present in amount between about 20 and 100 weight per cent of the amount of said 2-aminodiphenylamine.

5. The composition of claim 2 having incorporated therein an aliphatic ketone in amount between about 20 and 100 weight per cent of said 2-aminodiphenylamine.

6. The method of preventing instability of a hydrocarbon fuel containing as a principal antiknock ingredient tetraethyllead which comprises incorporating therein a stabilizing amount of a composition consisting essentially of 2-aminodiphenylamine in admixture with an aliphatic ketone, said 2-aminodiphenylamine present in amount between about 10 and about 50 weight per cent of such stabilizing composition.

7. In combination tetraethyllead and a stabilizing amount of a composition consisting essentially of 2-aminodiphenylamine in admixture with an aliphatic ketone, said 2-aminodiphenylamine present in amount between about 10 and about 50 weight per cent of such stabilizing composition.

8. A liquid stabilizing composition comprising in admixture 2-aminodiphenylamine and an aliphatic ketone, said 2-aminodiphenylamine present in amount between about 10 and about 50 weight per cent of such stabilizing composition.

9. The composition of claim 8 wherein said ketone is acetone.

References Cited in the file of this patent

UNITED STATES PATENTS

1,835,140	Calcott et al.	Dec. 8, 1931
2,410,829	Luten	Nov. 12, 1946