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AMYL DERIVATIVES OF LEAD AND THEIR PREPARATION

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This invention relates to amyl derivatives of lead and their preparation, the amyl derivatives specifically being mixed derivatives in which either different amyl radicals are attached to lead or one or more amyl radicals are attached to lead along with other alkyl or aryl radicals.

This application, with respect to the derivatives, is in part a continuation of my application Serial Number 333,512, filed January 18, 1929, to which reference may be made for methods of preparation alternative to that herein described.

The derivatives to which this application relates are found to be useful in preventing the knock of gasoline or other fuels, when used in high compression internal combustion engines, by raising their critical compressions to such an extent as to eliminate the objectionable detonation of the fuel mixture. The amyl derivatives have been found to be particularly effective in attaining this result, and of these the mixed amyl derivatives appear to be best.

It is the broad object of the present invention to provide such derivatives and a method of preparation therefor which is readily carried out on a large scale and which gives a high yield of the desired product, which, furthermore, contains colloidal lead as an advantageous product of the reaction.

More specific objects of the invention will be apparent from the following description in which there will first be set out a specific description of a preparation characteristic of those within the scope of the invention.

The preparation of dimethyldidiethylmethyl lead is chosen as an example, this compound having the formula: $(CH_3)_2((C_2H_5)_2CH)_2Pb$. It will be noted that the amyl radicals are diethylmethyl radicals.

The reaction is carried out under pressure in a vessel which is preferably a cylinder having a removable head at one end or a manhole at the side. Small valved pipes are arranged at the centers of the ends so as to act as shafts which are carried on bearings for the rotation of the cylinder, and which may be coupled to tubes for the introduction of gases under pressure or serve as connections to pressure gauges. The vessel is arranged so that it is partly immersed in a trough or tank in order that in its rotation during the reaction slightly less than one half of it comes into contact with a liquid (preferably a high boiling oil) which is maintained by the application of heat at such temperature that the contents are kept between 30° and 40° C.

Into the cylinder there is introduced between 350 and 360 parts of sodium-lead alloy containing 10% Na or between 370 and 380 parts of sodium-lead alloy containing 20% Na, the alloy being finely divided. To this are added 215 to 255 parts of diethylchlormethane, which may be obtained by halogenation of diethylmethane which occurs in natural gas or by the esterification by a halogen acid of diethyl carbinol. The cylinder head or manhole is then closed and one of the pipes is connected to a supply of methyl chloride which is introduced under pressure until a pressure gauge indicates that between 101 and 105 parts have been introduced. The charge is preferably so related to the size of the vessel that the initial pressure is in the neighborhood of 100 to 200 pounds per square inch. The valves are then closed and the vessel is slowly rotated in the heated liquid until the reaction is completed. The time required depends upon various factors such as the amount of charge and the temperatures. As the reaction is preferably carried out at low temperatures, the time may be from 12 to 24 hours. During the reaction the pressure drops as the methyl chloride enters into the reaction. The range of pressure and temperature is relatively immaterial so far as operativeness is concerned, the time required being alone affected.

If the entire amount of sodium-lead alloy is present at the beginning of the reaction as described above, the reaction may assume such initial violence as to produce a very high pressure in the reaction vessel. While small vessels may be readily designed to withstand such transient high pressures, it is desirable to avoid them in large vessels by adding the alloy intermittently in small quantities to the mixture of the other materials. This may readily be done without loss of the gaseous methyl chloride through the use of a valve arrangement adapted to first receive a charge of alloy while open to the atmosphere or supply and while closing the reaction vessel and adapted to then confine the charge of alloy and subsequently discharge it into the vessel.

When the reaction is completed the pressure is released, the cylinder opened, and the contents emptied into water. The water reacts with any remaining sodium which is preferably initially in excess of the theoretical amount. After washing several times with water to remove alkali and salts, the heavy dimethyldidiethylmethyl lead, containing colloidal lead, is filtered in order to remove metallic lead. The

compound containing the colloidal lead may then be separated from the water by means of separatory funnels. If it is desired to obtain the compound in a pure condition, free from colloidal lead, it is distilled in steam. Such separation from colloidal lead is neither necessary nor desirable if it is to be used in fuel since the colloidal lead, as well as the derivative, exerts considerable anti-knock effect.

Other methyl and amyl derivatives than the chlorides may be used in the above reaction, for example, the bromides, iodides, sulphates, etc. Also, the sodium-lead alloy may be replaced by other alkali or alkali earth metal-lead alloys or mixtures or metals such as magnesium or zinc may be used in admixture with lead to remove the acidic element or radical.

It might be expected that the above reaction would result in a mixture of tetraamyl lead and tetramethyl lead rather than the dimethyldiamyl lead. As a matter of fact, however, it is found that the mixed derivative is the primary product. This tendency to form mixed derivatives is found to be generally true, the radicals combining with the lead in proportions as near as possible to the molecular proportions of the halides or other derivatives in the original mixture.

As to variations of the above reaction with the resultant production of other derivatives, there may be produced tetraamyl lead derivatives in which the amyl groups are not all the same: for example there may readily be formed derivatives having the formula: $(R')(R'')_3Pb$ or $(R')_2(R'')_2Pb$ in which R' and R'' represent different amyl radicals, either, for example, being the radicals of normal amyl alcohol, of the ordinary amyl alcohols of commerce, i. e., isobutyl carbinol or secondary butyl carbinol, or of diethylcarbinol, referred to above. These derivatives may be readily prepared in a manner analogous to that described above, using the halide or other suitable ester derivatives in molecular proportions corresponding to the proportions of the radicals in the desired product.

Of the derivatives just mentioned, the best for the suppression of detonation appear to be those containing one, two or three diethylmethyl groups. In this connection it may be noted that tetradiethylmethyl lead appears more effective than the other tetraamyl lead derivatives and is within the scope of this invention. It is prepared in the manner described above using, however, only diethylchlormethane instead of a mixture of halide derivatives.

In a broader sense, it may be said that the invention relates to and includes the preparation of lead derivatives having the general formula R_4Pb in which at least two of the R's represent different radicals and in which one or more of the R's represent an amyl radical, which amyl radical is preferably diethylmethyl, although it wil be understood that the amyl radical may be any one of the isomeric C_5H_{11} groups. This generalization includes the mixed tetraamyl derivatives referred to above. Besides the above, there is within the scope of the invention the specific compound tetradiethyl methyl lead.

Those R's in the above formula, if any, which do not represent amyl groups may represent various alkyl or aryl radicals, for example methyl, ethyl, propyl, butyl, benzyl or such alkyl or aryl groups in which one or more hydrogens are replaced by organic or inorganic elements or radicals. There may thus be not only two but three or four different radicals attached to the lead. All of such derivatives may be readily formed by treating lead-sodium or equivalent alloy with alkyl or aryl halides or other suitable esters in admixture in proper molecular proportion with the amyl halide or sulphate or the like, the proportions of derivatives used corresponding to the proportions of the radicals in the lead derivative which it is desired to prepare.

In all of the preparations above described, more or less colloidal lead is found in the derivative obtained. As already stated this is a desirable constituent when the derivatives are used as detonation suppressing substances, which property all of the derivatives have in common. For the uses of these derivatives in admixture with fuel or as starting points for the preparation of colloidal lead reference may be made to my application Serial Number 333,512 referred to above.

What I claim and desire to protect by Letters Patent is:

1. A compound having the general formula R_4Pb in which the R's represent hydrocarbon radicals, at least one of which is a diethylmethyl radical.

2. A compound having the general formula R_4Pb in which the R's represent hydrocarbon radicals, at least two of which are different, and at least one of which is a diethylmethyl radical.

3. A compound having the general formula R_4Pb in which the R's represent hydrocarbon radicals, at least two of which are different, and at least two of which are diethylmethyl radicals.

4. A compound having the general formula R_4Pb in which the R's represent hydrocarbon radicals, at least two of which are different, and at least two of which are diethylmethyl radicals, the other being alkyl radicals.

5. Dimethyldidiethylmethyl lead.

6. The method of preparing a mixed amyl derivative of lead which includes the treatment of a mixture of hydrocarbon halides, the halides containing different hydrocarbon groups, at least one of which is an amyl derivative, with lead and a metal capable of uniting, in the reaction, with the acidic radicals of the alkyl derivatives.

7. The method of preparing a mixed amyl derivative of lead which includes the treatment of a mixture of hydrocarbon halides, the halides containing different hydrocarbon groups, at least one of which is a diethylmethyl derivative, with lead and a metal capable of uniting, in the reaction, with the acidic radicals of the alkyl derivatives.

8. The method of preparing a mixed amyl derivative of lead which includes the treatment of a mixture of alkyl halides containing different alkyl groups, at least one of which is an amyl derivative, with lead and a metal capable of uniting, in the reaction, with the acidic radicals of the alkyl derivatives.

9. The method of preparing a mixed amyl derivative of lead which includes the treatment of a mixture of alkyl halides containing different alkyl groups, at least one of which is a diethylmethyl derivative, with lead and a metal capable of uniting, in the reaction, with the acidic radicals of the alkyl derivatives.

10. The method of preparing a mixed amyl derivative of lead which includes the treatment of a mixture of alkyl halides containing different alkyl groups, at least one of which is an amyl halide, with lead and an alkali metal.

11. The method of preparing a mixed amyl derivative of lead which includes the treatment of

a mixture of alkyl halides containing different alkyl groups, at least one of which is a diethylmethyl halide, with lead and an alkali metal.

12. The method of preparing dimethyldidiethylmethyl lead which includes the treatment of a mixture of methyl chloride and diethylchlormethane in substantially equimolecular proportions with lead-sodium alloy.

13. The method of preparing dimethyldidiethylmethyl lead which includes the treatment of a mixture of methyl halide and diethylmethyl halide in substantially equimolecular proportions with lead-sodium alloy.

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