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PROCESS FOR MAKING TETRAMETHYL LEAD

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This invention relates to a process for the manufacture of tetramethyl lead, particularly by the reaction of a methyl halide with a sodium lead alloy in the presence of a catalyst.

It is well known that tetraalkyl lead compounds are useful as antiknock agents in fuels for internal combustion engines. Up to the present time, tetraethyl lead has been manufactured and used predominantly. However, tetramethyl lead, particularly because of its higher volatility, can be used advantageously as an antiknock agent in motor fuels, alone or in combination with tetraethyl lead and the like in varying proportions to improve the road performance of leaded fuels, as more fully described by Smyers et al. in U.S. Patent 2,310,376. Calingaert et al. in U.S. Patent 2,270,109, disclose a process for preparing a mixture of tetra-methyl and ethyl lead compounds by reacting a mixture of methyl chloride and ethyl chloride with sodium lead alloy in the presence of an aluminum type catalyst. Such process results in a mixture of five tetraalkyl lead compounds in which tetramethyl lead is present in a minor proportion. The process of Calingaert et al. does not constitute an economical process for making pure or substantially pure tetramethyl lead in large quantities and does not yield the combination of tetraalkyl lead compounds in the proportions required for many purposes disclosed by Smyers et al.

The manufacture of tetramethyl lead by the general alkyl halide-sodium lead alloy reaction requires special conditions. Whereas the ethyl chloride-sodium lead alloy system does not require catalysis and can be accelerated by such substances as ketones, alcohols, acetals, etc. known in the art, the methyl chloride-lead alloy system responds not at all or poorly to the presence of such accelerators and to conditions otherwise conducive to the formation of tetraethyllead. Methyl halides are unique in that only certain catalysts of the aluminum type seem effective to bring about the formation of methylated lead compounds. Even so, the aluminum type catalysts present practical difficulties in commercial scale operation. For example, an induction period is generally encountered before the methylation begins, when using the combination of aluminum alloy and aluminum chloride described by Calingaert et al. in U.S. Patent 2,270,109 for the manufacture of mixed methyl and ethyl leads from mixtures of methyl and ethyl chlorides. Also, relatively high temperatures (100° C.–110° C.) are required to achieve satisfactory yields of tetramethyl lead. The induction period and the high reaction temperature together present the hazard of sudden and uncontrollable reaction (i.e. surges in temperature and pressure) once the exothermic methylation begins. This can be particularly serious with tetramethyl lead because of the relative ease with which it can decompose explosively. Aluminum plus aluminum chloride catalysts are ineffective in at least one of the following respects, to avoid the induction period, to initiate reaction at low temperatures, to provide satisfactory reaction control, and to produce tetramethyl lead in good yield safely and in short time.

Other aluminum type catalysts suggested by Calingaert et al., for example, trimethyl aluminum, dimethyl aluminum chloride and the like, have the disadvantages for commercial use of being difficult and hazardous to handle

because of their extreme sensitivity to air and to moisture. On the other hand, it is desirable to be able to use aluminum chloride which is commercially available and presents no unusual storage and handling problems, provided satisfactorily high yields of tetramethyl lead can be obtained with it.

It is an object of this invention to provide a new and improved process for the manufacture of tetramethyl lead. Another object is to provide such a process which is particularly adapted for the large scale manufacture of pure or substantially pure tetramethyl lead. A further object is to provide a catalytic process for reacting a methyl halide with a sodium lead alloy wherein the reaction is initiated without an induction period and proceeds smoothly at relatively low temperatures to produce tetramethyl lead in good yield. A still further object is to provide a process for making tetramethyl lead which utilizes an aluminum halide catalyst in combination with an additional agent which materially improves the yield of tetramethyl lead. Other objects are to advance the art. Still other objects will appear hereinafter.

The above and other objects may be accomplished in accord with this invention which involves the process for making tetramethyl lead which comprises mixing at a temperature below 40° C. a sodium lead alloy, at least about 0.25 mole per mole of sodium of an alkylating agent which consists of a methyl halide in which the halogen has an atomic number in the range of 17 to 53, from about 0.05% to about 5% by weight of the alloy of an aluminum halide in which the halogen has an atomic number in the range of 17 to 53, and from about 0.1 to about 100 parts per part of the aluminum halide of a trialkyl aluminum in which each alkyl group contains 2 to 10 carbon atoms, heating the mixture to a temperature of from 40° C. to about 60° C. to initiate the methylation reaction, and then heating the mixture to a temperature of from 40° C. to about 130° C. and maintaining it at such temperature until the methylation reaction is substantially complete while gradually adding such quantities of said methyl halide as may be required to provide a total of at least one mole thereof for each mole of sodium.

It has been found that by carrying out the reaction in such manner, material advantages and improved results are obtained. By having the trialkyl aluminum present when the reaction mixture is subjected to reaction conditions, particularly to temperatures of from 40° C. to about 60° C., the reaction is initiated promptly without an induction period. In other words, the presence of the added trialkyl aluminum provides a smooth and safe initiation of the methylation reaction promptly at relatively low temperatures and ensures a smooth and controlled reaction. This is particularly important at the beginning when the mixture is heated to start the reaction. In addition, the use of the trialkyl aluminum to initiate the reaction also provides the unexpected benefit of increased yields of tetramethyl lead. This is all the more surprising, since the yields of tetramethyl lead are materially lessened when either the trialkyl aluminum or the aluminum halide is used in the absence of the other.

Broadly, the overall process comprises mixing the sodium lead alloy, the methyl halide, the aluminum halide catalyst, and a small proportion of trialkyl aluminum at a temperature below 40° C. at which the reaction does not readily take place, then heating the mixture with agitation to a temperature at which the reaction is initiated, maintaining the reaction mass at a temperature providing a reasonable rate of production of tetramethyl lead and, when the reaction is completed recovering the tetramethyl lead from the reaction mixture by conventional procedures. Preferably, when the reaction has become well

started, the temperature is gradually raised to one at which the reaction proceeds at a rapid rate, and completing the reaction at the higher temperature. Also, as is conventional in the preparation of tetraalkyl lead compounds by the reaction of alkyl halides with sodium lead alloys, the reaction is carried out under substantially anhydrous conditions and in the absence of air and oxygen, i.e. with anhydrous reactants while excluding air, oxygen, moisture and the like from the reactor, in the manner well known to the art. Reaction temperatures are usually in the range of from 40° C. to about 130° C. and, for reasons of safety, the pressure preferably should be kept below about 500 p.s.i.g., for example, by cooling, controlling the rate of heating and/or the amount of methyl halide in the reaction zone, and by venting. The reaction requires one mole of methyl halide for each mole of sodium in the sodium lead alloy. The reaction may be initiated with all of the desired amount of methyl halide present or with a fraction of the required amount of methyl halide present, followed by gradual addition of the rest of the desired amount as the reaction proceeds.

The alkylating agent employed will consist of a methyl halide in which the halogen has an atomic number in the range of 17 to 53, i.e. methyl chloride, methyl bromide, or methyl iodide, or a mixture of 2 or more methyl halides. Preferably, the reaction will be carried out with methyl chloride and monosodium lead alloy, NaPb. The total amount of methyl halide employed will be at least one mole and usually not more than 20 moles thereof per mole of sodium as sodium lead alloy, and preferably from about 2 to about 5 moles of methyl halide per mole of sodium. When it is desired to gradually add the methyl halide during the reaction, it is best to have present at the initiation of the reaction from about 0.25 to about 0.50 mole of methyl halide per mole of sodium, preferably about 0.50 mole, and to gradually add the rest of the methyl halide after the reaction has been initiated. Larger amounts than about 1.5 moles of the methyl halide can be used to dilute the reaction mass and aid in controlling the reaction temperature. Similarly, the methyl halide can be carried in an inert solvent, such as the hydrocarbons, hexane, benzene, toluene and the like, to dilute the reaction mass.

The process requires, as a catalyst, an aluminum halide in which the halogen has an atomic number in the range of 17 to 53. The term "aluminum halide" is used in its strict sense to mean the compounds which consist of aluminum and halogen, i.e. $AlCl_3$, $AlBr_3$, and AlI_3. Aluminum chloride is preferred. The aluminum halide can be used as such or as a suspension, slurry, or solution in an inert liquid carrier such as hexane, benzene, toluene, kerosene or liquefied methyl halide. Metallic aluminum and aluminum alloys may be used in combination with the aluminum halide catalyst as more particularly described by Calingaert et al. in U.S. Patent 2,270,109, but are unnecessary and usually are without significant advantage. The amount of the aulminum halide catalyst employed usually will be from about 0.05% to about 5% by weight of the sodium lead alloy, and preferably from about 0.5% to about 1.5%.

The trialkyl aluminum compounds, employed for initiating the reaction in the process of the present invention, are those in which each alkyl group contains from 2 to10 carbon atoms, and are well known to the art. They may be represented by the formula R_3Al wherein R represents an alkyl group and each R may be the same or different, but usually will be the same. Mixtures of 2 or more different trialkyl aluminum compounds may be used. Usually, the trialkyl aluminum compounds will be those in which each alkyl group contains 4 to 10 carbon atoms, i.e. butyl through decyl, and preferably branched primary alkyl groups, particularly those having at least one branch on the carbon atom beta to the aluminum, represented by triisobutyl aluminum, tri(2-ethylbutyl)aluminum, tri(2-ethylhexyl)aluminum, trioctyl aluminum, tri(2,5-dimethylheptyl)aluminum, and tridecyl aluminum. The trialkyl aluminum compounds, in which each alkyl group contains at least 4 carbon atoms, are very materially more practical than those in which the alkyl groups contain 2 to 3 carbon atoms because they are much less reactive towards air and moisture and hence are more safely and economically handled, e.g. if inadvertently exposed to air during normal handling, they tend to fume but do not burst into flame whereas the lower alkyl compounds tend to be spontaneously flammable in air, especially moist air. Trimethyl aluminum is so unstable and highly reactive to air and moisture that it is generally impractical to prepare and handle, and may not be shipped. On the other hand, triethyl aluminum, while highly reactive to air and moisture, is much more stable and may be shipped, and has the further advantage that it can be prepared economically from ethylene.

Usually and preferably from about 0.4 part to about 20 parts by weight of the trialkyl aluminum per part of aluminum halide catalyst will be used. Smaller amounts, down to about 0.1 part, of trialkyl aluminum per part of aluminum halide are beneficial. Amounts larger than about 20 parts of trialkyl aluminum, e.g. 100 parts or more thereof per part of aluminum halide, while operable, are generally unnecessary. In general, the larger amounts of trialkyl aluminum will be used with the lower amounts of aluminum halide and vice versa. For example, when 0.05% of aluminum halide is used, there usually will be used about 20–100 parts of trialkyl aluminum to each part of aluminum halide and, when the aluminum halide used is 2% or 5%, the trialkyl aluminum usually will be 0.4 or 0.1 part, respectively, for each part of aluminum halide. Also, the trialkyl aluminum can be used as such or added to the reaction mixture as a solution in an inert solvent, for example, as a solution of from about 20% to about 80% by weight thereof in a solvent, such as hexane, benzene, toluene, kerosene, and liquefied methyl halide.

It is essential for the purposes of this invention and to obtain the advantageous results thereof that the trialkyl aluminum be present in the reactor with the aluminum halide catalyst and the other components when the mixture is subjected to reaction conditions. Accordingly, at least part of the methyl halide and the other components are mixed at a temperature below 40° C., usually at room temperature or below, i.e. about 20° C. to about 30° C. and below, and then the mixture heated to the temperature required for initiation of the reaction. The methylation reaction can be initiated smoothly at temperatures of 40° C. to about 60° C., with temperatures not higher than about 60 °C. generally needed. The reaction can be completed at such temperatures. However, the reaction is undesirably slow and inefficient at such temperatures, and it is usually desirable to employ higher temperatures of from about 70° C. to about 130° C. for completion of the reaction. The production of tetramethyl lead proceeds at more reasonable rates and more efficiently at temperatures from about 70° C. to about 95° C. However, it is preferred to employ temperatures of from about 100° C. to about 110° C. for rapid completion of the reaction safely and maximum yields of tetramethyl lead.

The importance of these results is that a greater degree of safety is achieved and at a lower operating cost, considering the hazards and expense of using pressurized equipment and having a relatively unstable product such as tetramethyl lead confined at elevated temperatures. To be able to control temperatures and pressures is particularly important in the early stages of the reaction where the danger of a runaway reaction is greatest. Once at least 0.5 mole of methyl halide has reacted with the sodium lead alloy, the danger is greatly lessened and the temperatures can be more rapidly increased to the higher temperatures where the reaction takes place at the optimum rate. In general, the rate of heating and the pressure rise resulting therefrom are coordinated to prevent sharp increases therein, the temperature being raised grad-

ually to the desired maximum temperature. This gradual rise in temperature, if not too rapid, may be continuous from the temperature of mixing the ingredients through the reaction initiation stage to the temperature desired for rapid completion of the reaction, or may be intermittent, as desired.

The reaction is effected under agitation. It is usually desirable to carry out the reaction in the presence of an inert solid, such as graphite or silica, as an internal lubricant, mixing aid, or anti-agglomerant for lead, since ordinarily the reaction mass tends to be somewhat difficult to stir, probably due to the inherent tendency of the particles of free lead to stick together. From about 1% to about 20% by weight of the alloy are used, depending on the dimensions of the reactor, the effectiveness of the agitation means, and the proportions of the reactants.

In practice, the methyl halide is simply added to a reactor which will also contain the sodium lead alloy, aluminum halide, trialkyl aluminum, and usually an internal lubricant, such as graphite, at about room temperature. In a typical run, an autoclave is loaded at room temperature to contain 28 to 58 pounds (about 1.25 to about 2.5 moles per mole of sodium) of methyl chloride, 0.6 pound of $AlCl_3$, 0.6 pound of triisobutyl aluminum, and 3 pounds of graphite per 100 pounds of NaPb alloy, added in any order. Reaction is effected under agitation and pressure by heating to a temperature at which the methylation begins and can be maintained safely at a practical rate. The rate of heating and the pressure rise (as a result of heating) are coordinated to prevent sharp increases. Reaction mass temperature is controlled, by cooling the autoclave when necessary, to keep the internal pressure at a safe level, e.g. below about 300 p.s.i.g. Usually, a temperature of about 40° C.–60° C. has to be reached to initiate the methylation, and, once the exothermic reaction has started and is able to be controlled by the cooling means, the temperature is held at this temperature or is allowed to rise (or is raised) to 100° C.–110° C. and held there until the reaction is complete.

Alternatively, the methyl chloride can be fed gradually into the autoclave containing the other components. Preferably, about 0.25 to about 0.50 moles of methyl chloride per mole of sodium is added before the charge is brought to 40° C.–60° C. where reaction begins. The rest of the methyl chloride is then fed in slowly and the temperature allowed to increase to say 100° C.–110° C. where the reaction is completed. The pressure is kept under about 300 p.s.i.g. by cooling, controlling the methyl chloride feed, and venting of non-condensibles.

To recover the product, the charge is cooled to about 20° C.–30° C. and residual methyl halide vented to a recovery system, as in tetraethyl lead technology. The tetramethyl lead component can be recovered by solvent extraction, e.g. with toluene, or by steam distillation, according to the well-known methods.

In order to more fully illustrate this invention, preferred modes of carrying it into effect, and the advantageous results to be obtained thereby, the following examples are given in which the amounts and proportions are by weight, except where otherwise specifically indicated.

Example 1

A steel bomb is charged under nitrogen to contain 2.5 parts of graphite, 0.63 part of aluminum chloride, 100 parts of monosodium lead alloy and 1.25 parts of triisobutyl aluminum. Then, 77.5 parts of methyl chloride are added to the bomb cooled with solid carbon dioxide, which corresponds to a weight volume ratio of methyl chloride to total bomb capacity of 0.31 gram per cubic centimeter. After warming to room temperature, the bomb is heated to 50° C. in 8 minutes and held at 50° C. for 4 hours. Tetramethyl lead is obtained from the reaction mass in 51% yield on extraction with isooctane.

When the aluminum chloride is omitted, no tetramethyl lead is obtained under the above conditions. When the triisobutyl aluminum is omitted, the yield of tetramethyl lead is only 30%.

Example 2

The procedure of Example 1 is repeated except that 0.63 part instead of 1.25 parts of triisobutyl aluminum is used and the reaction mass, after warming to room temperature, is heated in 27 minutes to 110° C. and held there for 1 hour. The yield of tetramethyl lead is 88%.

In contrast, the yield of tetramethyl lead is not more than about 80% when either the aluminum halide or the trialkyl aluminum is used as the sole catalyst in this procedure. Also, when boron fluoride is used as the sole catalyst, no tetramethyl lead is obtained, in contrast to the disclosure (U.S. Patent 2,270,109) that this substance catalyzes the reaction of mixtures of methyl and ethyl halides with sodium lead alloy to produce mixed methyl and ethyl leads.

Example 3

The procedure of Example 1 is repeated except there are used 0.63 part instead of 1.25 parts of triisobutyl aluminum, methyl bromide instead of methyl chloride as methylating agent, and a reaction temperature of about 85° C. for 4 hours, to obtain tetramethyl lead in 76% yield.

Example 4

A stainless-steel lined pressure reactor is loaded in the following order with 3.4 parts of graphite, 0.62 part of $AlCl_3$, 100 parts NaPb alloy, 1.2 parts of triisobutyl aluminum and 90 parts of methyl chloride, the weight to volume ratio of the methyl chloride to the total capacity of the bomb corresponding to 0.21 gram/cc. The reaction mass, under agitation, is heated in 15 minutes to 70° C., held there for 3.5 hours, and cooled. The yield of tetramethyl lead, isolated by extraction with isooctane, is 77%.

Substantially the same results may be obtained on steam distilling the tetramethyl lead from the reaction mass.

When $AlCl_3$ is used alone in this procedure, the yield of tetramethyl lead is only 53% and, when the triisobutyl aluminum is the sole catalyst, the yield of tetramethyl lead is 69%.

Inferior results are obtained with aluminum chloride and aluminum turnings (e.g. as an alloy of composition 6.2–8.0 Cu, 1.4 Fe, 1–3 Si, 0.5 Mn, 0.07 Mg, 2.2 Zn, 0.3 Ni, 0.2 Ti, 0.5 other, the rest Al) as the sole catalyst combination under the above conditions. Induction periods of up to about 1 hour are observed before the reaction starts at about 70° C., and the yields of tetramethyl lead tend to be even lower than obtained with aluminum chloride alone. For example, the yield is 45.3% when 0.34 part of aluminum chloride and 0.21 part of the aluminum alloy are used as the catalyst.

Example 5

A 5 gallon autoclave is charged with 15,435 g. comminuted NaPb alloy, 454 g. graphite, 95 g. $AlCl_3$, 37.7 g. triisobutyl aluminum, and 4,220 g. methyl chloride (liquefied). The autoclave is sealed and the charge heated under agitation over a period of about one hour to 75° C., corresponding to a pressure of about 300 p.s.i.g., and then is heated over a period of 1.5 hours up to 112° C., during which time the maximum pressure was 300 p.s.i.g. The reactor is then cooled to about 25° C., vented, and the reaction mass discharged. The reactor is rinsed with 4 gallons of toluene and the rinsings also added to the product. The yield of tetramethyl lead is 84% by analysis.

Example 6

Example 5 is repeated using 15,757 g. of the NaPb alloy, 454 g. graphite, 97 g. $AlCl_3$, 88 g. triisobutyl aluminum, and 8,440 g. methyl chloride. The reaction mass is heated over a period of 1 hour to 70° C. and held at a tem-

perature within the range of about 80° C. to 95° C. to maintain a pressure of about 300 p.s.i.g., for 3 hours. Tetramethyl lead is obtained in 74% yield by steam distillation recovery.

Example 7

Example 6 is repeated except that there are used 85.7 g. instead of 88 g. triisobutyl aluminum, and the reaction mass is heated to 45° C. in 20 minutes (150 p.s.i.g.), then over the range 45° C. to 60° C. (maintaining an autoclave pressure of 150 p.s.i.g.) for 6 hours. The yield of tetramethyl lead is 68%.

Equally good results may be obtained in the preceding examples by employing in place of triisobutyl aluminum, an equivalent amount of one or more of tri(2-ethylbutyl)-aluminum, trioctyl aluminum, and tridecyl aluminum.

It will be understood that the preceding examples have been given for illustrative purposes solely and that this invention is not restricted to the specific embodiments described therein. On the other hand, it will be readily apparent to those skilled in the art that, subject to the limitations set forth in the general description, many variations can be made in the materials, proportions, conditions and techniques employed, without departing from the spirit and scope of this invention.

From the preceding description and examples, it will be apparent that this invention provides a new and improved process for making tetramethyl lead in high yields which process overcomes the difficulties and hazards involved in the prior processes. Particularly, this invention eliminates the induction period ordinarily encountered in prior processes and the hazards involved therein, and permits the initiation of the reaction at lower temperatures in a smooth and safe manner and the reaction to be readily controlled. It produces tetramethyl lead as the predominant product and makes it possible to safely and economically produce pure or substantially pure tetramethyl lead in high yields. Furthermore, this invention provides a process whereby tetramethyl lead can be readily obtained in materially higher yields than could be obtained heretofore. Accordingly, it will be apparent that this invention constitutes a valuable advance in and contribution to the art.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. The process for making tetramethyl lead which comprises mixing at a temperature below 40° C. a sodium lead alloy, at least about 0.25 mole per mole of sodium of an alkylating agent which consists of a methyl halide in which the halogen has an atomic number in the range of 17 to 53, from about 0.05% to about 5% by weight of the alloy of an aluminum halide in which the halogen has an atomic number in the range of 17 to 53, and from about 0.1 to about 100 parts per part of the aluminum halide of a trialkyl aluminum in which each alkyl group contains 2 to 10 carbon atoms, heating the mixture to a temperature of from 40° C. to about 60° C. to initiate the methylation reaction, and then heating the mixture to a temperature of from 40° C. to about 130° C. and maintaining it at such temperature until the methylating reaction is substantially complete while gradually adding such quantities of said methyl halide as may be required to provide a total of at least one mole thereof for each mole of sodium.

2. The process for making tetramethyl lead which comprises mixing at a temperature below 40° C. a sodium lead alloy, from about 0.25 to about 20 moles per mole of sodium of an alkylating agent which consists of a methyl halide in which the halogen has an atomic number in the range of 17 to 53, from about 0.05% to about 5% by weight of the alloy of an aluminum halide in which the halogen has an atomic number in the range of 17 to 53, and from about 0.4 to about 20 parts per part of the aluminum halide of a trialkyl aluminum in which each alkyl group contains 4 to 10 carbon atoms, heating the mixture to a temperature of from 40° C. to about 60° C. to initiate the methylation reaction, and then heating the mixture to a temperature of from 40° C. to about 130° C. and maintaining it at such temperature until the methylating reaction is substantially complete while gradually adding such quantities of said methyl halide as may be required to provide a total of at least one mole thereof for each mole of sodium.

3. The process for making tetramethyl lead which comprises mixing at a temperature below 40° C. a sodium lead alloy, from about 0.25 to about 20 moles per mole of sodium of an alkylating agent which consists of a methyl halide in which the halogen has an atomic number in the range of 17 to 53, from about 0.05% to about 5% by weight of the alloy of an aluminum halide in which the halogen has an atomic number in the range of 17 to 53, and from about 0.4 to about 20 parts per part of the aluminum halide of a trialkyl aluminum in which each alkyl group is a branched primary alkyl group of 4 to 10 carbon atoms, heating the mixture to a temperature of from 40° C. to about 60° C. to initiate the methylation reaction, and then heating the mixture to a temperature of from about 70° C. to about 110° C. and maintaining it at such temperature until the methylating reaction is substantially complete while gradually adding such quantities of said methyl halide as may be required to provide a total of at least one mole thereof for each mole of sodium.

4. The process for making tetramethyl lead which comprises mixing at a temperature below 40° C. monosodium lead alloy, from about 0.25 to about 5 moles per mole of sodium of an alkylating agent which consists of methyl chloride, from about 0.5% to about 1.5% by weight of the alloy of aluminum chloride, and from about 0.4 to about 20 parts of triisobutyl aluminum per part of aluminum chloride, heating the mixture to a temperature of from 40° C. to about 60° C. to initiate the methylation reaction, and then heating the mixture to a temperature of from about 70° C. to about 110° C. and maintaining it at such temperature until the methylating reaction is substantially complete while gradually adding such quantities of methyl chloride as may be required to provide a total of from about 2 to about 5 moles thereof for each mole of sodium.

5. The process for making tetramethyl lead which comprises mixing at a temperature below 40° C. a sodium lead alloy, from 1 to about 20 moles per mole of sodium of an alkylating agent which consists of a methyl halide in which the halogen has an atomic number in the range of 17 to 53, from about 0.05% to about 5% by weight of the alloy of an aluminum halide in which the halogen has an atomic number in the range of 17 to 53, and from about 0.4 to about 20 parts per part of the aluminum halide of a trialkyl aluminum in which each alkyl group contains 2 to 10 carbon atoms, heating the mixture to a temperature of from 40° C. to about 60° C. to initiate the methylation reaction, and then heating the mixture to a temperature of from 40° C. to about 130° C. and maintaining it at such temperature until the methylating reaction is substantially complete.

6. The process for making tetramethyl lead which comprises mixing at a temperature below 40° C. a sodium lead alloy, from 1 to about 20 moles per mole of sodium of an alkylating agent which consists of a methyl halide in which the halogen has an atomic number in the range of 17 to 53, from about 0.05% to about 5% by weight of the alloy of an aluminum halide in which the halogen has an atomic number in the range of 17 to 53, and from about 0.4 to about 20 parts per part of the aluminum halide of a trialkyl aluminum in which each alkyl group contains 4 to 10 carbon atoms, heating the mixture to a temperature of from 40° C. to about 60° C. to initiate the methylation reaction, and then heating the mixture to a temperature of from 40° C. to about 130° C. and maintaining it at such temperature until the methylating reaction is substantially complete while gradually adding such quantities of said methyl halide as may be required to provide a total of at least one mole thereof for each mole of sodium.

maintaining it at such temperature until the methylating reaction is substantially complete.

7. The process for making tetramethyl lead which comprises mixing at a temperature below 40° C. monosodium lead alloy, from 1 to about 5 moles per mole of sodium of an alkylating agent which consists of methyl chloride, from about 0.5% to about 1.5% by weight of the alloy of aluminum chloride and from about 0.4 to about 20 parts per part of aluminum chloride of a trialkyl aluminum in which each alkyl group is a branched primary alkyl group of 4 to 10 carbon atoms, heating the mixture to a temperature of from 40° C. to about 60° C. to initiate the methylation reaction, and then heating the mixture to a temperature of from about 70° C. to about 110° C. and maintaining it at such temperature until the methylating reaction is substantially complete.

8. The process for making tetramethyl lead which comprises mixing at a temperature below 40° C. monosodium lead alloy, from 1 to about 5 moles per mole of sodium of an alkylating agent which consists of methyl chloride, from about 0.5% to about 1.5% by weight of the alloy of aluminum chloride, and from about 0.4 to about 20 parts of triisobutyl aluminum per part of aluminum chloride, heating the mixture to a temperature of from 40° C. to about 60° C. to initiate the methylation reaction, and then heating the mixture to a temperature of from about 70° C. to about 110° C. and maintaining it at such temperature until the methylating reaction is substantially complete.

9. The process for making tetramethyl lead which comprises initiating at a temperature of from about 40° C. to about 60° C. the reaction of a sodium lead alloy and an alkylating agent which consists of a methyl halide in which the halogen has an atomic number in the range of 17 to 53 in the presence of from about 0.05% to about 5% by weight of the alloy of an aluminum halide in which the halogen has an atomic number in the range of 17 to 53 and from about 0.1 to about 100 parts per part of aluminum halide of a trialkyl aluminum in which each alkyl group contains 2 to 10 carbon atoms, then heating the mixture to a temperature of from about 40° C. to about 130° C. and maintaining the mixture at the latter temperature until the methylation reaction is substantially complete.

10. The process for making tetramethyl lead which comprises initiating at a temperature of from about 40° C. to about 60° C. the reaction of a sodium lead alloy and an alkylating agent which consists of a methyl halide in which the halogen has an atomic number in the range of 17 to 53 in the presence of from about 0.05% to about 5% by weight of the alloy of an aluminum halide in which the halogen has an atomic number in the range of 17 to 53 and from about 0.4 to about 20 parts per part of aluminum halide of a trialkyl aluminum in which each alkyl group is a branched primary alkyl group of 4 to 10 carbon atoms, then heating the mixture to a temperature of from about 70° C. to about 110° C. and maintaining the mixture at the latter temperature until the methylation reaction is substantially complete.

11. The process for making tetramethyl lead which comprises initiating at a temperature of from about 40° C. to about 60° C. the reaction of a sodium lead alloy and an alkylating agent which consists of methyl chloride in the presence of from about 0.05% to about 1.5% by weight of the alloy of aluminum chloride and from about 0.4 to about 20 parts of triisobutyl aluminum per part of aluminum chloride, then heating the mixture to a temperature of from about 70° C. to about 110° C. and maintaining the mixture at the latter temperature until the methylation reaction is substantially complete.

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