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HERBERT W. DAUDT, OF CARNEYS POINT, NEW JERSEY, ASSIGNOR TO E. I. DU PONT DE NEMOURS & COMPANY, OF WILMINGTON, DELAWARE, A CORPORATION OF DELAWARE

ALKYLATED LEAD

No Drawing. Application filed October 15, 1927. Serial No. 226,529.

This invention relates to the preparation of alkylated lead and more particularly to the production of such a compound at substantially atmospheric pressure.

The preparation of tetra ethyl lead by the action of alkyl halides on lead-sodium alloys has been accomplished and disclosed in a number in instances. In Ann. d. Chem. 84,308 (1853); Jour. Prak. Chem. 60,304 (1853) Löwig disclosed a method for the preparation of tetra ethyl lead by heating alloys of sodium and lead with ethyl iodide at the boiling point of the ethyl iodide, a reflux condenser being used to condense and return the ethyl iodide boiled off. It was thought that the iodide was essential to this reaction.

According to one authority, Ghira, Gazz. Chim. Ital. 24 (1) 42 (1894), this reaction requires the presence of small amounts of water. More recent developments indicate that the reaction between ethyl bromide and lead-sodium alloys to form tetra ethyl lead will not take place in the absence of water. It is also being shown conclusively in the co-pending application of K. P. Monroe, Serial No. 701,641, filed March 25, 1924, that water or some other hydroxylic compounds, such as alcohol, must be present in order to induce the desired reaction.

The ethyl bromide process recently developed, and disclosed in British Patent 216,083 of 1925, includes as its essential feature the progressive addition of water over long periods of time to a mixture of ethyl bromide and alloy. The temperature maintained is slightly lower than the boiling temperature of ethyl bromide, and the equipment for carrying out the reaction includes a reflux condenser. The reaction also requires the presence of a catalyst, such as pyridine or dimethyl-aniline.

In the British Patent 214,221 of 1925 to Krauss and Callis, it was found, an entirely different and unexpected condition existed when ethyl bromide or ethyl chloride was heated with lead-sodium alloys under pressure and at temperatures above their normal boiling points, i. e., boiling point under atmospheric pressure conditions. Under these conditions Krauss and Callis found that no water or hydroxylic compound is required. Their process, so far as concerns the use of the chloride, has been found to be successfully operative on a large scale. The disclosure of this British patent covers the preparation of not only tetra ethyl lead, but also that tetra alkyl lead compounds in general. However, the process disclosed in this British Patent 214,221 requires the use of pressure and of temperature above the boiling points.

The process of British Patent 214,221 to Krauss and Callis is, however, entirely different from the process of British Patent 216,083 of 1925 to General Motors, the latter requiring the use of water and of tertiary amine as catalysts. In fact, the addition of these two compounds is of decided disadvantage in the Krauss and Callis process. Furthermore, different alloys are best suited for these processes. The Krauss and Callis process requires almost a 10% sodium alloy, (British Patent 214,221) while the General Motors process (British Patent 216,083) uses any alloy containing 15–18% of sodium. In British Patent 214,221 to Krauss and Callis the difficulties inherent in the tendency for the development of excess temperature and pressure were recognized and were overcome by means of the temperature depending upon the interrupted addition of the alkyl chloride to the alloy contained in an autoclave, as disclosed in U. S. Patent 1,612,131, dated December 28, 1926.

In the co-pending application of Calcott, Parmelee and Lorriman, Serial No. 146,063 filed November 3, 1926, the addition of potassium to the alloy for the purpose of increasing the yield of tetra ethyl lead has been disclosed.

An object of my invention is to induce the reaction between alkyl chloride and lead-sodium alloy under such conditions that neither the use of water and tertiary amine, nor the use of pressure should be necessary. A further object of my invention is to eliminate the excess temperature sometimes obtainable, particularly with the process disclosed in British Patent 214,221, with resulting losses in yield of tetra ethyl lead.

I have succeeded in inducing the reaction

between ethyl chloride and the alloy at the normal boiling temperature (12° C.) of the ethyl chloride and at even lower temperatures. Thus, I have been able to eliminate the use of pressure and of temperatures above the boiling point. I can carry out the reaction in pressureless equipment at the boiling temperature with the use of a reflux condenser to condense and return the ethyl chloride boiled off, or, I can conduct it at a temperature below the boiling point of ethyl chloride.

With a pure lead-sodium alloy the reaction at these low temperatures is very slow and only a low yield of tetra ethyl lead is obtained.

But the addition of potassium to the alloy facilitates the reaction to such an extent that excellent yields can be obtained at these low temperatures. The use of 0.75%–1.50% potassium in the alloy has enabled me to obtain yields of 75–85% of tetra ethyl lead.

The conducting of the reaction under a reflux condenser has a very decided advantage, that of cooling even the interior portions of the reacting mass. By allowing the ethyl chloride to boil, the heat required by the vaporization is withdrawn from any portion of the charge where contact with ethyl chloride is maintained, and where the temperature has been raised to the boiling point of the liquid. By means of a suitable condensing equipment this heat is permanently removed from the system.

The tetra ethyl lead may be removed from the completed reaction mass by steam distillation, or by extraction with a suitable solvent.

The ethyl chloride may be mixed with an inert solvent, such as benzene, toluene, gasoline and kerosene. Such mixtures have higher boiling temperatures than has ethyl chloride and they, therefore, allow the use of higher temperatures than the boiling point of pure ethyl chloride.

The alloy used in this work contained 10% sodium and 90% lead, excepting where the sodium was replaced in small amounts by its equivalent of potassium.

While I have referred to tetra ethyl lead in particular, in describing my invention, it will be understood that I contemplate using the process in connection with the preparation of tetra alkyl lead compounds, with the possible exception of tetra methyl lead. In the case of the latter it may be that the reaction would not take place at the normal boiling temperature (−23.7°C.) of methyl chloride.

In the case of some of the higher alkyl chlorides, their normal boiling temperatures are very likely higher than their reacting temperatures with lead-sodium alloys and so far as is known the prior art does not disclose the ideal conditions for preparing the corresponding tetra alkyl lead. These conditions do not, however, affect the preparation of tetra alkyl lead compounds by my new procedure. The following examples illustrate actual embodiments of my invention, but it is to be understood that these are illustrative only and are not to be taken as in any way limiting my invention.

Example A.—To a vessel, provided with a brine cooled reflux condenser, add 60 parts of ethyl chloride and 100 parts of sodium lead alloy containing 10% sodium. Reflux at the boiling temperature for 24 hours. Drown the charge in 300 parts of water and distill off the tetra ethyl lead with steam.

Example B.—To a vessel, provided with a brine cooled condenser, add 50 parts of ethyl chloride and 100 parts of sodium-potassium-lead alloy containing 9.1% sodium and 1.5% potassium. Reflux at the boiling temperature for six hours. Drown the charge in 300 parts of water and distill off the tetra ethyl lead with steam.

Example C.—In a vessel agitate a mixture of 50 parts of ethyl chloride and 100 parts of sodium-potassium-lead alloy containing 9.1% sodium and 1.5% potassium for 16 hours, maintaining a temperature of 8–10° C. for the entire period. Drown the charge in 300 parts of water and distill off the tetra ethyl lead with steam.

Example D.—In a vessel agitate a mixture of 20 parts of toluene, 50 parts of ethyl chloride, and 100 parts of an alloy containing 10% sodium and 90% lead for 20 hours, maintaining a temperature of 19–22° C. for the entire period. Drown the charge in water and distill with steam. After the oil, being distilled, becomes heavier than the water coming over with it, change the receiver and collect the rest of the oil as tetra ethyl lead.

Example E.—In a vessel agitate a mixture of 50 parts kerosene, 20 parts of ethyl chloride and 65 parts of an alloy containing 9.4% sodium, 0.8% potassium and 89.8% lead for twelve hours, maintaining a temperature of 21–23° C. for the entire period. Extract the tetra ethyl lead from the finished reaction mass with gasoline.

Example F.—To a vessel, provided with a reflux condenser, add 90 parts of n-butyl chloride and 100 parts of sodium-potassium-lead alloy containing 9.1% sodium and 1.5% potassium. Reflux at the boiling temperature for 8 hours. Drown the charge in 300 parts of water, add 50 parts of sodium chloride, and distill off the tetra- (n) butyl lead with steam.

Example G.—To a vessel, provided with a reflux condenser, add 100 parts of iso-propyl chloride and 100 parts of sodium-potassium-lead alloy containing 9.1% sodium and 1.5% potassium. Reflux at the boiling temperature for 5 hours. Extract the tetra-iso-propyl lead with benzene.

As many apparently widely different embodiments of this invention may be made without departing from the spirit thereof, it is to be understood that I do not intend to limit myself to the specific embodiments thereof except as indicated in the appended claims.

I claim:

1. A process for making an alkylated lead which comprises effecting a reaction solely between an alloy of lead with at least one alkali metal, and an alkyl chloride, at substantially atmospheric pressure.

2. A process for making an alkylated lead which comprises effecting a reaction between an alloy of lead with a mixture of alkali metals, and an alkyl chloride, at substantially atmospheric pressure.

3. A process for making a compound PbR_4, in which R is an alkyl group containing from two to four carbon atoms, which comprises effecting a reaction solely between an alloy of lead with at least one alkali metal, and an alkyl chloride containing not more than four carbon atoms, at substantially atmospheric pressure.

4. A process for making a compound PbR_4, in which R is an alkyl group containing from two to four carbon atoms, which comprises effecting a reaction between an alloy of lead with a mixture of alkali metals, and an alkyl chloride containing not more than four carbon atoms, at substantially atmospheric pressure.

5. A process for making a compound PbR_4, in which R is an alkyl group containing from two to four carbon atoms, which comprises effecting a reaction between an alloy of lead with a mixture of sodium and potassium, and an alkyl chloride containing not more than four carbon atoms, at substantially atmospheric pressure.

6. A process for making lead tetra ethyl which comprises effecting a reaction between ethyl chloride and an alloy of lead, sodium, and potassium, at substantially atmospheric pressure.

7. A process for making lead tetra ethyl which comprises effecting a reaction between ethyl chloride and an alloy of lead, sodium, and potassium, at substantially atmospheric pressure, and at a temperature approximating the boiling point of ethyl chloride.

8. A process for making lead tetra ethyl which comprises effecting a reaction between ethyl chloride and an alloy of lead, sodium, and potassium, at substantially atmospheric pressure, and at the boiling temperature of the reaction mixture, condensing the vaporized ethyl chloride and returning it to the reaction vessel.

9. A process for making a compound PbR_4, in which R is an alkyl group containing from two to four carbon atoms, which comprises effecting a reaction solely between an alloy of lead with at least one alkali metal, and an alkyl chloride containing not more than four carbon atoms, at substantially atmospheric pressure, and in the presence of a diluent.

10. A process for making a compound PbR_4, in which R is an alkyl group containing from two to four carbon atoms, which comprises effecting a reaction between an alloy of lead, sodium, and potassium, and an alkyl chloride containing not more than four atoms, at substantially atmospheric pressure, the ratio of lead to sodium in the alloy being approximately 10:1 and the ratios of sodium to potassium being between the limits 20:1 and 7:1.

11. A process for making tetra ethyl lead, which comprises effecting a reaction solely between an alloy of lead with at least one alkali metal, and ethyl chloride, at substantially atmospheric pressure and in the presence of a diluent.

12. A process for making tetra ethyl lead which comprises effecting a reaction between an alloy of lead, sodium, and potassium, and ethyl chloride, at substantially atmospheric pressure, the ratio of lead to sodium in the alloy being approximately 10:1 and the ratio of sodium to potassium being between the limits 20:1 and 7:1.

13. The process of producing tetra ethyl lead which comprises inducing a reaction between ethyl chloride and a lead-sodium alloy containing potassium at the normal boiling temperature of ethyl chloride.

In testimony whereof I affix my signature.

HERBERT W. DAUDT.