Patented Feb. 4, 1936 2,029,301

UNITED STATES PATENT OFFICE

2,029,301

PROCESS OF PREPARING TETRA ALKYL LEAD

Louis S. Bake, Pennsgrove, N. J., assignor to E. I. du Pont de Nemours & Company, Wilmington, Del., a corporation of Delaware

No Drawing. Application June 9, 1933, Serial No. 675,089

12 Claims. (Cl. 260—11)

In the present commercial manufacture of organic lead compounds and particularly of alkyl lead compounds, an alkyl halide is contacted with a lead mono-sodium alloy in an autoclave at temperatures starting at about 30 to 40° C. The lead mono-sodium alloy employed in this process, up to the present time, has ordinarily been prepared by melting together the lead and sodium, then pouring into molds, cooling, and then grinding. The particle size of alloy thus prepared varies from about 40 mesh and smaller, to pieces of about ½ inch or more in diameter admixed with considerable amounts of the alloy in the form of dust.

While high yields of alkyl lead compounds have been obtained by this process, the yields have not proved to be entirely satisfactory and the reaction has not proceeded as smoothly as desired. I have found that the yield of alkyl lead compound varies in accordance with the particle size and physical condition of the alloy and the presence or absence of appreciable amounts of alloy in the form of dust.

The object of this invention is to provide a process for preparing tetra alkyl lead whereby higher yields of the compound may be produced. Other objects are to provide new compositions of matter and to advance the art. Still other objects will appear hereinafter.

These objects may be accomplished in accordance with my invention which comprises preparing and employing a lead mono-sodium alloy in the form of small uniformly sized substantially dust-free particles preferably not larger than about ⅛ inch and also preferably larger than about 3/32 inch in diameter. By "uniform", I mean that the smallest particle must not be less than about ½ the size of the largest particle. Such alloy may be obtained by various methods.

In the grinding of lead mono-sodium alloy, as in other materials, a considerable proportion is reduced to dust which, on account of the enormously increased surface area, is extremely sensitive to the action of oxygen and moisture in the air forming, among other things, caustic soda. As a result, a considerable proportion of the very finely divided alloy is decomposed and lost and, at the same time, the caustice soda introduced into the reaction mass of lead sodium alloy and ethyl chloride has a marked deleterious effect on the reaction. Fine alloy or dust that has been exposed to the atmosphere appears to become coated with the decomposition products, which products prevent ready contact of the ethyl chloride with the pure alloy within the particles. Accordingly, these coated particles react very slowly, if at all. It is also probable that the larger particles become coated with the decomposition products of the smaller particles thereby decreasing the efficiency of contact between the larger particles and the ethyl chloride. Dust that has not been exposed and become coated with decomposition products is abnormally reactive and, as a result, the reaction with ethyl chloride is so rapid that it is very difficult to control the temperature of the reaction mass. Large pieces of alloy, on the other hand, present only a small surface area for contact with ethyl chloride and hence react very slowly and inefficiently.

I have found that uniformly sized particles of about 3/32 inch to about ⅛ inch in diameter and which are substantially free from dust are far more stable against slight exposure to air than is dust and will react with ethyl chloride and the like in a smooth manner with increase in the production of tetra alkyl lead and permit ready control of the temperatures. These uniformly sized particles greatly decrease the loss of alloy and prevent the introduction of impurities into the alkyl lead autoclave.

Such uniformly sized particles may be obtained by sieving ordinary ground alloy. However, this method is expensive and difficult to operate as it involves the steps of casting, grinding and sieving. It is practically impossible to prevent access of air in the grinding and sieving operations and consequent loss of alloy due to decomposition. Also a large proportion of the alloy must be remelted, reground and resieved.

I have also discovered a method whereby dust-free uniformly sized particles may be more readily obtained without the disadvantages attending the grinding and sieving as above described. This new method comprises cooling a molten lead mono-sodium alloy, with stirring, to a temperature below that at which particles of the alloy tend to adhere to each other. By this process, the alloy assumes the form of uniformly sized crystals of octahedral structure or the form of well polished particles. When alloy, thus produced, is employed in the preparation of alkyl lead compounds, particularly in the preparation of tetraethyl lead, the yield of the alkyl lead compound is materially increased.

It would ordinarily be expected that, if a lead mono-sodium alloy is prepared in a molten state and stirred until it cools well below its freezing point, the alloy would freeze the agitator. I have found this not to be the case. I have found that, if molten lead mono-sodium alloy is stirred at

a very slow rate of speed until the alloy is cooled to below 300° C., the alloy forms particles of almost perfect uniformly sized crystals of octahedral structure. By stirring at a very slow rate of speed, I mean stirring at a rate such that the agitator is barely moving. Such stirring may be done by hand or by mechanical means, if desired.

If rapid stirring is employed, the edges of the crystals, as they are formed, are rounded off by the friction of agitation with the result that, instead of crystals of octahedral structure being obtained, the alloy is formed as well polished particles. Alloy prepared by this more rapid stirring of the molten alloy will be hereinafter termed grained alloy. By rapid stirring I mean something on the order of 10 to 30 times as rapid as the slow stirring previously referred to. There is necessarily a definite mechanical limit to the rate at which an agitator can be run when working with materials of this kind, which limit varies with the type of vessel or agitator employed and the size of charge treated. In a conventional crystallizing kettle, for example, the agitator will generally run at about 15 revolutions per minute. This, I have found, is very satisfactory for my purpose in preparing the grained alloy.

Since the hot alloy has a great affinity for moisture it should be maintained in an atmosphere of a dry oxygen free inert gas during the cooling and stirring operation. From a safety and economic standpoint, nitrogen is to be preferred for this purpose. However, if desired, other inert gases such as hydrogen, helium and the like may be employed.

The alloy freezes at about 371° C. Crystals are formed upon cooling to only a few degrees below the freezing point with stirring. These crystals have a wet appearance and, if the stirring is discontinued at this point, the particles of alloy tend to adhere to each other and are difficult, if not impossible, to separate, resulting in a conglomerate mass that offers no advantage over ordinary large lumps of alloy. However, if the stirring is continued until the temperature of the alloy reaches about 300° C., or less, the particles have a dry appearance and do not tend to adhere together. Thus the stirring may be stopped when the alloy reaches about 300° C.; or when it has this dry appearance. However, I preferably continue the stirring until the alloy reaches a temperature of 275° C. or less, as a safety factor. Continued stirring below this point does not result in any material advantage but merely results in rounding the edges of the crystals to a greater extent.

This last method of obtaining uniformly sized particles of the alloy is generally to be preferred over the process of grinding and sieving as it is cheaper to operate and there is less loss in material. It is also much more difficult to prevent exposure of the alloy to the atmosphere during grinding and sieving operations, hence a purer and more satisfactory alloy may be obtained according to my preferred method.

In order to more clearly illustrate my invention and the advantages thereof the following example is given:

Example

Lead mono-sodium alloy was prepared in four different forms as follows:

(A) Cast alloy, ground to irregular particle size of ¼ inch and less.

(B) Ground alloy passed through a 40 mesh screen.

(C) A single solid piece of alloy.

(D) Grained alloy of uniform size of $\frac{3}{32}$ to $\frac{5}{32}$ inch particle size obtained by rapidly stirring molten alloy until cooled to about 275° C.

100 grams of each of the above alloys A, B, C and D were reacted with 50 cc. of ethyl chloride in an autoclave under identical conditions such as are ordinarily employed for this reaction. The alloy and ethyl chloride were maintained in contact until reaction was complete. The yield in tetraethyl lead obtained with alloy D, was several percent higher than that obtained with any of the other alloys.

My alloy has the advantages of increasing the yield of alkyl lead compound, rendering the operation much smoother, making it easier to control the temperature of the reaction, is easier to handle and has a less tendency to oxidize in the atmosphere than alloy prepared in any other manner.

While I have disclosed specific methods for preparing my new alloy and its use in the preparation of tetraethyl lead it will be readily understood by those skilled in the art that variations and modifications may be made in such processes and the alloy may be employed for preparing other organic lead compounds without departing from the spirit of my invention. Accordingly, the scope of my invention is to be limited solely by the appended claims, construed as broadly as is permissible in view of the prior art.

I claim:

1. The process for preparing tetra alkyl lead which comprises contacting under reacting conditions, an organic halide with a lead mono-sodium alloy in the form of small substantially dust-free particles of a uniform size.

2. The process for preparing tetra alkyl lead which comprises contacting under reacting conditions, an organic halide with a lead mono-sodium alloy in the form of small substantially dust-free particles of a uniform size of about $\frac{1}{32}$ to about ⅛ inch in diameter.

3. The process for preparing tetraethyl lead which comprises contacting, under reacting conditions, ethyl chloride with a lead mono-sodium alloy in the form of small substantially dust-free particles of a uniform size.

4. The process for preparing tetraethyl lead which comprises contacting, under reacting conditions, ethyl chloride with a lead mono-sodium alloy in the form of small substantially dust-free particles of a uniform size of about $\frac{1}{32}$ to about ⅛ inch in diameter.

5. The process for preparing tetra alkyl lead which comprises contacting, under reacting conditions, an organic halide with a lead mono-sodium alloy in the form of small uniformly sized crystals of octahedral structure.

6. The process for preparing tetra alkayl lead which comprises contacting, under reacting conditions, an organic halide with a lead mono-sodium alloy in the form of small substantially dust-free crystals of octahedral structure of a uniform size of about $\frac{1}{32}$ to about ⅛ inch in diameter.

7. The process for preparing tetra alkyl lead which comprises contacting, under reacting conditions, an organic halide with a lead mono-sodium alloy in the form of small substantially dust-free crystals of octahedral structure of a uniform size and having their edges rounded off and their surfaces well polished.

8. The process for preparing tetra alkyl lead which comprises contacting, under reacting conditions, an organic halide with a lead mono-sodium alloy in the form of small substantially dust-free crystals of octahedral structure of a uniform size of about $\frac{1}{32}$ to about $\frac{1}{8}$ inch in diameter and having their edges rounded off and their surfaces well polished.

9. The process for preparing tetraethyl lead which comprises contacting, under reacting conditions, ethyl chloride with a lead mono-sodium alloy in the form of small substantially dust-free crystals of octahedral structure of a uniform size.

10. The process for preparing tetraethyl lead which comprises contacting, under reacting conditions, ethyl chloride with a lead mono-sodium alloy in the form of small substantially dust-free crystals of octahedral structure of a uniform size of about $\frac{1}{32}$ to about $\frac{1}{8}$ inch in diameter.

11. The process for preparing tetraethyl lead which comprises contacting, under reacting conditions, ethyl chloride with a lead mono-sodium alloy in the form of small substantially dust-free crystals of octahedral structure of a uniform size and having their edges rounded off and their surfaces well polished.

12. The process for preparing tetraethyl lead which comprises contacting, under reacting conditions, ethyl chloride with a lead mono-sodium alloy in the form of small substantially dust-free crystals of octahedral structure of a uniform size of about $\frac{1}{32}$ to about $\frac{1}{8}$ inch in diameter and having their edges rounded off and their surfaces well polished.

LOUIS S. BAKE.