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MANUFACTURE OF LEAD COMPOUNDS

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This invention relates to the manufacture of alkyllead compounds. More particularly, the invention relates to a new and improved process for the manufacture of tetramethyllead.

Alkyllead compounds have for some time been known and widely used for antiknock additives to fuels for internal combustion engines. Tetraethyllead has been most common but tetramethyllead is highly advantageous and particularly effective in certain instances. This has given rise to the need for efficient processes for the manufacture of tetramethyllead.

It has long been known that tetramethyllead can be made by the reaction of monosodium lead alloy, NaPb, usually in a flaked or otherwise highly subdivided form, with the methylating agent, methyl chloride, in a reaction autoclave under elevated temperature and pressure conditions. However, because of significantly different physical properties, of tetraethyllead, and tetramethyllead, considerable problems occurred in establishing commercial operations for making tetramethyllead. It has been disclosed in Cook and Sistrunk Patent 3,049,558 that the problems of manufacture of tetramethyllead can be largely overcome by conducting the reaction of monosodium lead alloy and methyl chloride under certain conditions and in the presence of inert hydrocarbon liquids in certain proportions. It was shown by Cook and Sistrunk that by the use of their procedure, that high yields were obtained, and that the properties of the resultant product, which included tetramethyllead plus the inert hydrocarbon diluent, were very conductive to safe operation and safety of the resultant product, as well as greatly facilitating the synthesis of the tetramethyllead. The essential feature of the Cook et al. process is the synthesis of the tetramethyllead in a reaction medium of a certain class of inert hydrocarbons.

While the Cook et al. procedure fully solved many of the manufacturing problems, nevertheless it necessarily resulted in the presence of a substantial amount of inert hydrocarbon material accompanying the tetramethyllead, which material was carried through to final antiknock compositions sold to the consuming refining and petroleum product blending purchasers. Thus, this particular product is diluted material, in that the inert hydrocarbon diluent does not add any marked antiknock effectiveness characteristic to the tetramethyllead, but nevertheless imposes an economic charge in that it must be transported, stored, shipped and otherwise represents a charge on the sale and consumption of tetramethyllead as an antiknock.

Antiknock compounds or mixtures using tetramethyllead as the antiknock ingredient have also included substantial proportions of later added dihaloethane components provided as scavengers for the mixture in its use in gasolines. These scavengers are ethylene dibromide and ethylene dichloride, which are used in proportions of roughly about 18 percent of the final mixture.

An object of the present invention is to provide a new and improved process for the manufacture of tetramethyllead. More particularly, an object of the invention is to provide a new and novel process for the preparation of

tetramethyllead accompanied by an active component normally provided in final antiknock mixtures using tetramethyllead. An additional object of certain highly effective embodiments of the invention is to provide a tetramethyllead producing process wherein the use of an inert hydrocarbon reaction medium component can be eliminated or drastically reduced if desired.

The process of the present invention involves carrying out the reaction of monosodium lead alloy and methyl chloride at known reaction conditions of temperature and pressure, and with known feed and other operating techniques, and in the presence of a catalyst, and also involves the use of a quantity of 1,2-dichloroethane as a component of the reaction mixture. Very surprisingly it is found that, although 1,2-dichloroethane will readily react with monosodium lead alloy at reaction conditions, nevertheless, tetramethyllead can be made in good yields even if the 1,2-dichloroethane is present.

In all forms of the process, the feed or charge of monosodium lead alloy to the process is accompanied by a reaction medium of from about 10 to 25 weight percent, including at least about 8 percent 1,2-dichloroethane. An inert liquid hydrocarbon can, if desired, be used, but is not essential, and is not normally used above a concentration of about 10 percent. Thus, when no hydrocarbon component is used, 1,2-dichloroethane is used in proportions of from about 10 to 25 percent. The concentrations expressed above, and elsewhere herein, are as weight percents base on the alloy charge, except if otherwise stated.

The inert liquid hydrocarbons which can be used, as well as the 1,2-dichloroethane, should be free of entrained or dissolved moisture. Generally, the hydrocarbon component, if used is a compound or cut or mixture, having a mid-boiling point of about 90 to 150° C. Illustrative materials include toluene, xylenes, n-heptane, n-octane, 3-ethyl hexane, 2-methyl hexane, 3-methyl hexane, 2,6-dimethyl heptane, butylene alkylate mixture, having a mid-boiling point of 103° C., isooctane (2,2,4-trimethyl pentane) and others. One preferred class of embodiments involves the use of 8 to 15 percent 1,2-dichloroethane, with from 2 to 10 percent toluene.

In carrying out the process generally, the reaction procedure is similar to that heretofore used. A quantity of monosodium lead alloy is charged to a reaction autoclave, along with the 1,2-dichloroethane, and, when desired, the inert diluent hydrocarbon. At the same time, a catalyst is provided, typical catalysts being trimethyl aluminum, triethyl aluminum, or methyl aluminum sesquichloride, other catalysts being known in the art. The charge components are heated and methyl chloride is added gradually. The reaction is usually carried out at means temperatures of 70 to 130° C. and under the autogenous pressure of the reacting system. The methyl chloride is provided in total proportions of at least 1 mole per atom of sodium in the alloy charged and up to about 5 moles. Upon the completion of the reaction, the excess pressure is vented and the reactor and contents are cooled, as a result of the venting and also through applying cooling to the autoclave heat transfer surfaces. The reaction product mixture, or reaction mass, is then discharged for a recovery operation, which is commonly the steam distillation of the tetramethyllead containing product. The reaction mass includes not only the tetramethyllead, the 1,2-dichloroethane, and, when used, an inert diluent hydrocarbon, but also includes sodium chloride obtained from the reaction as a joint chemical product, and substan-

tial quantity of subdivided lead which is the result of the reaction, expressed by the following equation:

$$4CH_3Cl+4NaPb \rightarrow (CH_3)_4Pb+3Pb+4NaCl$$

The recovery operation distills the tetramethyllead and other accompanying normally liquid materials from the reaction mass which as shown includes lead solids and sodium chloride components.

Other details of the mode of carrying out the reaction are shown in the art as in Tullio Patent 3,072,695 and Cook and Sistrunk, 3,049,558.

To illustrate the best mode of carrying out the process of the invention, the following working example describes typical and highly effective operations wherein the dichloroethane employed is the sole reaction medium provided.

EXAMPLE 1

Monosodium lead alloy flakes are charged to a reaction autoclave in proportions of about 25 pounds per cubic feet of reaction space. Several percent of graphite are provided as an internal lubricant for the agitation of the reaction to be conducted. Also charged is 1,2-dichloroethane in proportions of about 10.3 percent, and trimethyl aluminum, in the proportions of about 0.2 weight percent of aluminum. The reactor and contents are heated to approximately 80° C. and liquid methyl chloride feed is then started, reaction occurring promptly as shown by a further rise in the operating temperature. The pressure is also allowed to rise, and is controlled at the autogenous pressure corresponding to a controlled reaction temperature of about 80–90° C. The temperature is controlled by cooling of the autoclave and by refluxing of the volatile components, principally the methyl chloride, by means of reflux condensers. The methyl chloride feed is continued as required, an excess of up to 100 percent being provided. The reaction requires several hours, termination of reaction being shown by a steadily dropping temperature and pressure.

When the reaction is thus completed, the autoclave and contents are cooled and subsequently the excess pressure is released by venting. The reaction mass is then discharged to a steam distillation vessel, wherein the tetramethyllead and 1,2-dichloroethane are steam distilled from the other components of the reaction mixture. The tetramethyllead containing product so recovered is a mixture with 1,2-dichloroethane. The product is about one-fifth to two-fifths, by weight, 1,2-dichloroethane, dependent on the individual batch yields of the tetramethyllead and the efficiency of recovery.

As previously indicated, when desired the dichloroethane employed can be supplemented by quantities of inert diluent hydrocarbon, as in the following working example.

EXAMPLE 2

The same procedure, as in the preceding example, is again followed, except that the 1,2-dichloroethane is reduced to a concentration of 8 percent, and dry toluene is charged in proportions of about 2.1 percent. The same operations are carried out. A high yield of tetramethyllead is achieved, the product including from one-sixth to one-third by weight 1,2-dichloroethane depending on efficiency of recovery and yields of individual batches. The toluene also appears in the product in proportions of 7 or 8 percent.

Additional examples are given in the following table. In Examples 3–6, methyl aluminum sesquichloride was used as catalyst, in proportions of 1 percent of the alloy charge. In the other examples, other aluminum type catalysts in similar concentrations are used.

Charge Additives—Weight Percent of Alloy

Example	1,2-Dichloroethane	Hydrocarbon	Comments
3	14.2	Toulene, 8.7	TML Yield, 32.6.
4	14.2	Toluene, 8.7	Percent TML, 53.4.
5	14.2	None	Percent TML, 61.8.
6	14.2	None	Percent TML, 62.5.
7	22	Ethylbenzene, 4	
8	19	3-ethyl hexane, 10	
9	14	Aromatic petroleum cut, mid-B.P. 110° C.	
10	13.5	Toluene, 5	
11	9.5	Isooctane, 1	
12	10	o-Xylene, 6	

From the foregoing examples, it is seen that substantial variation of the invention can be employed and good results will be achieved. To illustrate the surprising effectiveness of the process, compared with the normal expected results from the presence of 1,2-dichloroethane at reaction conditions, the following comparative examples are given.

COMPARATIVE EXAMPLE A

A charge of alloy was introduced to the same autoclave as used in Examples 3–6, and in addition the autoclave was charged with dichloroethane in proportions of 14 weight percent based on the alloy and 8.7 weight percent toluene. The mixture was then processed by heating at 100° C. for one hour. Analysis of the resultant product showed that inorganic chloride was present equivalent to 88 percent of the sodium of the alloy charged.

COMPARATIVE EXAMPLE B

The same procedure as in comparative Example A was followed, except that no toluene was provided to the reaction mixture. Analysis of the mixture after the heating period showed that inorganic chloride had been formed corresponding to about 90 percent of the original sodium of the alloy.

From the foregoing experiments, it is seen that under the operating conditions employed in the present process, it would be expected that the dichloroethane would result in degradation of a large segment of the sodium of the sodium lead alloy employed. In contrast, good yields of the desired tetramethyllead product are achieved.

I claim:

1. In the manufacture of tetramethyllead by the catalyzed reaction of monosodium lead alloy and methyl chloride, the improvement consisting of reacting in the presence of a reaction medium of from about 10 to 25 weight percent based on the alloy, said reaction medium including at least 8 percent 1,2-dichloroethane, and from 0 to about 10 weight percent of an inert liquid hydrocarbon having an atmospheric mid-boiling point of from about 90 to 150° C.

2. In the manufacture of tetramethyllead by the catalyzed reaction of monosodium lead alloy and methyl chloride, the improvement consisting of reaction in the presence of a reaction medium consisting essentially of 1,2-dichloroethane in the proportions of from about 10 to 25 weight percent based on the alloy.

3. In the manufacture of tetramethyllead by the catalyzed reaction of monosodium lead alloy and methyl chloride, the improvement consisting of reacting in the presence of a reaction medium consisting essentially of toluene in the proportions of from about 2 to 10 weight percent of the alloy and 1,2-dichloroethane in the proportions of about 8 to 15 weight percent of the alloy.

No references cited.