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MANUFACTURE OF ALKYLLEAD COMPOUNDS

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This invention relates to the preparation of alkyllead compounds such as tetraethyllead.

Tetraethyllead is by reason of its wide use, a very important alkyllead compound and in the past has been made by the reaction of ethyl chloride with an alloy of 10 per cent sodium and 90 per cent lead by weight (50 atom per cent sodium). The reaction is carried out under pressure and at an elevated temperature of 75 to 90° C. in an autoclave in which the reactants are stirred or agitated. Upon completion of the reaction, excess or unreacted ethyl chloride is vented off, and the reaction products are discharged into water in a still. The tetraethyllead is then separated by steam distilling from the other reaction products. Other alkyllead compounds are prepared in the same way, using the appropriate alkylating agent.

While this process has been commercially successful, it has several marked disadvantages. A principal disadvantage is its restriction to the use of a sodium-lead alloy of very critical composition, if good yields are to be obtained. Thus, a sodum-lead alloy having a sodium content as little as ½ per cent away from the 10 per cent value, gives a sharply lower yield of alkyl-lead compound when the alkylation is conducted under presently employed commercial operating conditions.

The alloy is ordinarily made by fusing together suitable amounts of lead and sodium, followed by cooling, then grinding the mass of solidified alloy thus produced to the particle size suitable for the subsequent alkylation and storing the ground product in an inert atmosphere till needed.

A further difficulty of the conventional alkylation process is the fact that the reaction mixture, upon completion of the reaction, contains relatively large amounts of metallic lead which has a tendency to ball up and in general makes the extraction of the desired alkyllead product quite cumbersome. Furthermore, since this lead represents an appreciable fraction of the cost of manufacture, economy dictates that it be separately recovered, purified and re-used. The significance of this prior art difficulty will be better appreciated when it is considered that approximately three-fourths of the lead used in the prior art alkylation of the type described above must be so recovered and re-used.

A still further difficulty with the prior commercial operations is that they have been limited to using alkyl chlorides as alkylating agents and as a result the alkylations must be effected under highly elevated pressures in order to carry out the reaction at the required temperatures with

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the alkylation agent in liquid form. For the high pressures thus necessitated the alkylation vessel must be of extremely rugged construction and is quite cumbersome in operation. Furthermore, there is considerable danger that a flaw in the reaction vessel may cause it to fail during the reaction, thereby endangering any personnel or other apparatus that is nearby.

In addition to the above, the prior commercial process using sodium-lead alloys converts the sodium to sodium chloride, a by-product that is substantially valueless and also introduces a corrosion problem.

Among the objects of the present invention is the provision of novel methods for preparing alkyllead compounds which largely overcome the above and related disadvantages.

A further object of the present invention is the provision of a novel process for effectively alkylating a sodium-lead alloy with alkylating agents other than alkyl chlorides.

According to the present invention, it has been discovered that a sodium-lead alloy having a composition in the range corresponding to between about 20 and 22 weight per cent sodium is effectively alkylated with an alkyl sulfate or an alkyl phosphate alkylating agent when the reaction is carried out in a temperature range of 110° C. to 150° C. Many attempts have been made to utilize alloys in this range for the manufacture of tetraethyllead because of the attractive economics possible from employing an alloy containing approximately twice the amount of sodium present in the currently employed NaPb alloy. Heretofore, little success has been achieved. In particular the conventional alkylating agent, ethyl chloride, reacts with great difficulty with such alloys, and, surprisingly, ethyl bromide is even less reactive.

The reaction is further improved by conducting it in the presence of an iodine catalyst and/or a thermal stabilizer for the alkyllead product. Preferred examples of suitable iodine catalysts are PbI_2, elemental iodine, sodium iodide, potassium iodide, methyl iodide, ethyl iodide, iodobenzene, mercuric iodide and cuprous iodide. Other iodine catalysts that are not quite as effective are CdI_2, CeI_3, BiI_3, CsI, ZnI_2, AsI_5, SbI_5, and n-propyl iodide.

Thermal stabilizers for alkyllead compounds are described in the copending Calingaert U. S. patent application, Serial No. 64,259, filed December 8, 1948, now abandoned, and the contents of that application are hereby incorporated in the present specification as though fully set forth therein.

It is noted that the thermal stabilizers described in the above application include fused ring and unsaturated compounds that have boiling points at least as high as 1° C. at atmospheric pressure, and examples of which are naphthalene, styrene, crotonaldehyde, allo-ocimene, butadiene, diamylene, dipentene, trimethylethylene, divinylbenzene, cyclohexene, dicyclopentadiene, allyl iodide, chloroprene, hexachloropropylene, ethynylcyclohexanol, tiglic alcohol, 2,2'-azonaphthalene, 2-benzeneazo-1-naphthylamine, allyl isothiocyanate, anthracene, chrysene, naphthalene, alphamethyl naphthalene, bromonaphthalene, chloronaphthalene, alphanaphthol, betanaphthol, naphthoresorcinol, tetrahydronaphthalene, indene and naphthoquinoline.

Other stabilizers shown in the above application include hydroxy compounds or substances that readily generate such compounds. Glyceryl monostearate, glycol dilaurate, 2-nitro-2-methyl-1-propanol, phloroglucinol, resorcinol, 2,4,6-tri-(dimethyl-aminomethyl) phenol, 2-methyl-2,4-pentanediol, ethylene bromohydrin, ethanolamine and furfuryl alcohol are examples of this type of stabilizer. To the above list there can be also added nitro compounds, including nitrates, nitrites, amino derivatives and azo compounds, as for example alloxan, azobenzene, n-butyl nitrate, n-butyl nitrite, nitroethane, nitromethane, p-nitrobenzoic acid, p-nitroaniline, acetyl aminothiophene, p,p'-diaminodiphenylmethane and furfuryl amine. Other stabilizers mentioned in the earlier application are halogen-containing compounds, stearyl iodide and styrene dibromide.

Of the above stabilizers the most effective appear to be naphthalene and styrene. However, the general class of unsaturated hydrocarbons, particularly aryl-substituted olefins, as well as other unsaturated compounds, fused ring hydrocarbons, and halogen-containing compounds, nitro compounds, nitrates, nitrites, azo compounds, amino derivatives and hydroxy compounds, any of which have boiling points at least as high as 1° C. at atmospheric pressure and that are soluble in the alkyllead compound appear to be effective as thermal stabilizers.

The alloys of the present invention are conveniently made by fusing a mixture of metallic sodium and metallic lead in the desired proportions, and cooling the fused product. The reaction is preferably performed with the alloy reduced as by crushing to a particle size of 8 to 20 mesh, although smaller particles are also highly effective. The use of particles coarser than about 8 mesh generally slows down the reaction somewhat and is not ordinarily desired.

As one specific example of the present invention wherein all parts and percentages are by weight, 100 parts of 8 to 20 mesh sodium-lead alloy containing 21.7 per cent sodium and the balance lead was added to 2.5 times the stoichiometric amount of diethyl sulfate (calculated on the basis of the sodium present in the alloy), and one part of lead iodide along with 0.75 part naphthalene. The mixture was held in a container from which the air was flushed by a stream of nitrogen, the container was sealed and heated to a temperature of 140° C. for five hours. At the end of this time, the container was permitted to cool to a temperature of approximately 25° C. and the reaction mixture poured into water and steam distilled to recover the tetraethyllead that was formed. The yield of tetraethyllead was 89 per cent based on the sodium content of the alloy.

If in the example the thermal stabilizer or the iodine catalyst is omitted, the yield is reduced to an appreciable extent. However, even with both the thermal stabilizer and the iodine catalyst eliminated, yields of almost 40 per cent based on the sodium content of the alloy used can be obtained, but this is preferably done at temperatures no higher than about 130° C. Any of the above-listed iodine catalysts will increase the yield, however, to about 60 per cent when used in amounts from ½ per cent to 5 per cent based on the total weight of the sodium-lead alloy. The thermal stabilizers are also helpful when used without iodine catalysts, particularly at reaction temperatures higher than 130° C. In general, however, such reactions are best conducted for shorter periods of time, about 3 to 4 hours being the maximum preferred duration of this type of reaction. As indicated in the above Calingaert application, the thermal stabilizers are very effective in concentrations of from about 0.1 per cent to about 5 per cent based on the amount of alkyllead compound formed. In any event, the reaction appears to proceed effectively for at least about 3 hours regardless of the particular additives or temperatures used, so that this is a preferred minimum reaction time.

Below about 110° C. the above reaction takes place to somewhat a limited extent which is impractical for commercial operation. Above about 150° C. it appears that lead alkyls are efficiently formed but are subsequently decomposed before they can be recovered, so that the final yield is penalized. The high temperature decomposition is apparently the result of some chemical reaction, presumably with the alkylating agent, and is not any reflection on the stabilizing effect of the purely thermal stabilizers.

It is not necessary to use extremely pure diethyl sulfate in the above reaction; practical grades appear to give just as good yields. Alkylation results similar to the above example are obtained with other alkyl sulfates such as dimethyl sulfate, di-N-propyl sulfate, di-isobutyl sulfate, mixed sulfates such as methyl-ethyl sulfate, and ethyl-isopropyl sulfate. Alkyl phosphates have also been found to be suitable alkylating agents in accordance with the present invention, producing alkyllead yields that are quite high, although lower than that produced by the alkyl sulfates. Examples of such alkyl phosphates are triethyl phosphate, trimethylphosphate, tri-n-propyl phosphate, methyldiethyl phosphate, etc.

It is usually advisable to keep the alkyl sulfate or alkyl phosphate alkylating agent concentration from being excessively high inasmuch as they appear to attack and destroy some of the formed alkyllead compounds, especially when the reaction runs to more than 3 hours at temperatures above 130° C. A maximum alkylating agent concentration of about 3 stoichiometrical proportions based on the equation given above is suitable. If the alkylating agent is reduced to below 1.25 of the stoichiometrical amount, the yield begins to suffer somewhat.

A feature of the present invention is the fact that the sodium-lead proportions in the reacting alloy are not unduly critical. Thus, alloys containing as low as 20 weight per cent and as high as 22 weight per cent sodium can be employed advantageously, and our preferred range is between about 20.0 and 21.7 weight per cent sodium.

In addition to the 21.7 per cent sodium alloy employed in the above example with a diethyl

sulfate agent alkylating agent substantially the same result is obtained when alloys containing 20.0, 20.5 and 22 weight per cent sodium are employed with diethyl sulfate as in the above example. Likewise other typical methods of conducting the process of our invention comprise treating such sulfate alkylating agents as methylethyl sulfate, dimethyl sulfate dipropyl sulfate, methylpropyl sulfate, di-n-butyl sulfate and the like with the foregoing typical alloys. Furthermore, the above and other similar alloys within the preferred range of our process can be employed with the phosphate alkylating agents with equally good results, that such phosphate alkylating agents include for example trimethyl phosphate, triethyl phosphate, tri-N-propyl phosphate, methyldiethyl phosphate, diethylbutyl phosphate and the like.

A further feature of the present invention is that, as shown in the equation given above, less than half of the lead in the original alloy remains unalkylated, assuming the reaction goes to completion. In other words, the reaction is theoretically capable of alkylating more than 50 per cent of the lead in the alloy, whereas the prior commercial technique can only alkylate one-fourth of the original lead.

Instead of recovering the formed alkyllead compounds by steam distillation, as indicated above, they can be separated by fractional distillation, either at atmospheric or reduced pressure. The decreased amount of lead in the final reaction mixture simplifies such fractional distillation. Where the alkyllead compound is distilled over at temperatures higher than about 110° C., it is advisable to effect the distillation in the presence of a thermal stabilizer. In addition, where the alkyllead product is fractionally distilled the residue which is largely a mixture of lead, sodium-alkyl sulfate or phosphate, and unreacted alkylating agent, can then be worked up to separate the lead and convert the sodium alkylsulfate content back to di-alkylsulfate or trialkyl phosphate so that it can be reused.

As many apparently widely different embodiments of this invention may be made without

departing from the spirit and scope hereof, it is to be understood that the invention is not limited to the specific embodiments hereof, except as defined in the appended claims.

We claim:

1. A process for the manufacture of tetraethyllead which comprises reacting a sodium-lead alloy containing between about 20 and 22 weight per cent sodium with undiluted diethyl sulfate at a temperature of between about 110° to 150° C. and in the presence of a minor amount of naphthalene and a catalyst comprising lead iodide.

2. A process for the manufacture of tetraethyllead which comprises reacting a sodium-lead alloy containing between about 20 and 22 weight per cent sodium with undiluted diethyl sulfate at a temperature of between about 110° to 150° C. and in the presence of a minor amount of styrene and a catalyst comprising lead iodide.

3. A process for the manufacture of alkyllead compounds comprising treating a sodium lead alloy containing between about 20 and 22 weight percent sodium with an undiluted alkylating agent selected from the class consisting of alkyl sulfates and alkyl phosphates at a temperature of about 110° to 150° C. and in the presence of a thermal stabilizer for the alkyllead compound produced.

4. The method of claim 3 wherein an iodide catalyst is employed.

5. A process for the manufacture of tetraethyllead which comprises treating a sodium lead alloy containing between about 20 and 22 weight percent sodium with undiluted diethyl sulfate at a temperature of between about 100–150° C. and in the presence of a thermal stabilizer for the tetraethyllead until a substantial proportion of tetraethyllead is produced and recovering said tetraethyllead from the reaction mixture.

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