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RECOVERY OF ALKYL LEAD COMPOUNDS

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This invention relates to the recovery of alkyl lead compounds from their reaction masses and more particularly to the recovery of tetra ethyl lead from its reaction mass by steam distillation.

In the present day commercial processes for manufacturing alkyl lead compounds and particularly tetra ethyl lead, a lead monosodium alloy is contacted with an alkyl halide such as ethyl chloride in a reaction chamber. The reaction mixture thus obtained comprises an intimate mixture of unreacted lead sodium alloy, sodium chloride, lead and the alkyl lead compound. There is 2½ to 3 times as much solid material comprising sodium chloride, lead and unreacted lead-sodium alloy as there are alkyl lead compounds. The alkyl lead compound is adsorbed upon the particles of lead. This reaction mixture has the appearance of wet sand from which the alkyl lead compound cannot be removed by any method such as decantation or filtration.

In the commercial process, this reaction mass is introduced into a relatively large volume of water, the mixture agitated and steam passed therethrough to drive off the lead alkyl compounds by steam distillation. This method of recovering the alkyl lead from the reaction mass has not proved to be entirely satisfactory for the reason that substantial proportions of the alkyl lead compound remain adsorbed on the lead particles which also tend to agglomerate. This adsorbed and occluded alkyl lead compound cannot be removed by extending the time of the distillation.

In order to improve the recovery of the lead alkyl compound from the reaction mass it has been proposed to add, to the reaction mass in the still, wetting and dispersing agents which prevent agglomeration of the lead in the mass and permit a more complete recovery of the alkyl lead compound. While this latter process has proved to be very successful in operation, it has been found that substantial amounts of the alkyl lead compounds are not removed from the reaction mass but remain adsorbed upon the particles of lead. The lead sludge remaining from such a process will normally contain from 1 to 4% of the alkyl lead compound adsorbed on the lead.

An object of the present invention is to provide a new method for recovering alkyl lead compounds from reaction masses or lead sludges containing the same. A still further object is to provide a process whereby almost theoretical recovery of alkyl lead compounds are obtained from the reaction masses. Other objects are to advance the art. Still other objects will appear hereinafter.

These objects may be accomplished in accordance with our invention which comprises neutralizing either wholly or partially the alkali in the reaction mass or lead sludge and then distilling by steam in accordance with the usual process.

We have found that, when an acid reacting substance is added to a reaction mass or lead sludge, containing alkyl lead compounds, in such amounts that the alkalinity of the reaction mass or sludge is reduced to a pH of not lower than 7 and then the reaction mass or lead sludge is subjected to steam distillation in accordance with the usual custom, almost theoretical recovery of the organic lead compound is obtained. Among the acid reacting substances which we have found to operate most satisfactory for our purposes are sulfuric acid, acetic acid, phthalic acid, ammonium sulphate, ammonium acetate and the like.

Preferably, the acid reacting substances should be employed in an amount sufficient to reduce the alkalinity of the reaction mass or sludge to a pH of between 7 and 8. However, smaller amounts of the acid reacting substances may be employed and we have found that satisfactory results may be obtained when sufficient of the acid reacting substances is employed to reduce the pH of the reaction mass or sludge to between 7 and 11. It is undesirable to reduce the pH of the reaction mass or sludge to below 7.0 as the excess acid tends to decompose the alkyl lead compounds although complete removal of the alkyl lead compound from the reaction mass or lead sludge may be obtained by employing excess of the acid reacting substance.

The acid reacting substance may be added to the reaction mass at the start of or during the distillation or at the end of a straight steam distillation followed by further distillation to remove the alkyl lead compound released from the sludge by coagulation of the lead.

In order to more clearly illustrate our invention, the preferred mode of carrying the same into effect and the advantageous results to be obtained thereby, the following examples are given:

Example 1

100 parts of a reaction mass, obtained by reacting ethyl chloride with monosodium lead alloy, was added to 300 parts of water and the mixture distilled with steam in the usual manner. Upon analysis, it was found that 8.4 parts or 8.4% of tetra ethyl lead remained in the lead sludge.

Example 2

100 parts of a reaction mass, similar to that treated in Example 1, was added to 300 parts of water containing 0.2 part of Turkey red oil. This mixture was then subjected to steam distillation in the usual manner. Upon analysis, it was found that 3.2 parts or 3.2% of tetra ethyl lead was retained by the sludge.

Example 3

100 parts of a reaction mass, similar to that treated in Example 1, was added to 300 parts of water. Dilute sulfuric acid was added to the resulting mixture in an amount sufficient to reduce the pH of the mixture to 7.5. The resulting mixture was subjected to steam distillation in the same manner as in Examples 1 and 2. After distillation, it was found that only 0.16 part or 0.16% of tetra ethyl lead remained in the lead sludge.

Example 4

100 parts of a reaction mass, similar to that treated in Example 1, was added to 300 parts of water. To the resulting mixture, was added sulfuric acid in an amount sufficient to reduce the pH to 9.3. This mixture was then subjected to steam distillation as in the preceding examples. After such distillation, it was found that the lead sludge retained 0.35% of tetra ethyl lead.

Example 5

The experiment of Example 3 was repeated except that ammonium sulfate was employed in place of the sulfuric acid. As a result, 0.19% of tetra ethyl lead was retained in the sludge.

Example 6

The experiment of Example 4 was repeated employing ammonium sulfate in place of the sulfuric acid. The lead sludge, remaining after the distillation, contained 0.26% tetraethyl lead.

Example 7

100 parts of a reaction mass, similar to that treated in Example 1, was added to 300 parts of water. Acetic acid was then added to the resulting mixture until the pH was reduced to 7.5 and the resulting mixture subjected to steam distillation in the usual manner. After distillation, it was found that 0.17% of tetraethyl lead remained in the sludge.

Example 8

The experiment of Example 7 was repeated employing a smaller amount of acetic acid so that the pH of the mixture was reduced to only 9.3. After distillation, 0.42% tetraethyl lead was found to have been retained by the lead sludge.

Example 9

A reaction mass, obtained by reacting ethyl chloride with monosodium lead alloy, was subjected to a steam distillation. After distillation, it was found that the still residue or lead sludge contained 2.9% of tetraethyl lead. 100 parts of this still residue or sludge was redistilled. After such redistillation, 2.7% of tetraethyl lead was found in the sludge. Another 100 parts of the still residue or sludge, containing 2.9% of tetra ethyl lead, was slightly acidified with sulfuric acid and then redistilled with the removal of all but 0.09% of the tetra ethyl lead from the sludge.

From the above examples, it will be apparent that the acid reacting substances and the amounts thereof employed may be rather widely varied. Other acid reacting substances which may be mentioned are hydrochloric acid, butyric acid, oleic acid, stearic acid, sulfonic acids and the like.

The acid reacting substances may be employed either with or without wetting and dispersing agents. For example, an alkyl lead reaction mass may be added to water and then the pH of the mixture adjusted by means of the acid substances or the reaction mass may be added to water containing wetting and dispersing agents such as are disclosed in Patent 1,645,375 issued to Daudt et al. and the copending application of Downing, Parmelee, Pedersen and Stecher, Serial No. 597,800 filed on or about March 9, 1932 and the pH adjusted by adding an acid substance. In other words, the processes disclosed in the aforesaid patent and application may be employed modifying them by adding acid substances in accordance with our invention. Among the wetting and dispersing agents disclosed by Daudt et al. and which may be employed in our process are glue, agar-agar, Turkey red oil, engine oil, lard oil, benzene, toluene, sodium sulfide, sodium carbonate, sodium sulfate, sodium sulfite, sodium sulfite and engine oil, and the like. Downing et al. in their application above identified disclose as wetting and dispersing agents engine oil and thiocarbanilide, sodium chromate, sodium dichromate, sodium thiosulfate, sodium silicates, sulfonated castor oils as Turkey red oil and monopole oil, salts of alkyl naphthalene sulfonic acids, condensation products of naphthol sulfonic acids and formaldehyde, reaction products of oleic acid and aliphatic diamines, the higher fatty and unsaturated acid and their soaps, resinates, and the like which may be employed in our process.

From the foregoing description of our invention it will be readily apparent to those skilled in the art that many changes and modifications may be made in the process and the ingredients employed without departing from the spirit of our invention. Accordingly, the scope of our invention is to be limited solely by the appended claims construed as broadly as is permissible in view of the prior art.

We claim:

1. The process of recovering tetra alkyl lead from a reaction mass containing the same and unreacted lead-sodium alloy which comprises mixing the reaction mass with water, steam distilling the mixture, mixing with the distillation residue an acid reacting compound sufficient in amount to materially reduce the alkalinity of the mixture to a pH of not lower than 7.0 and then redistilling the partially neutralized mixture with steam.

2. The process of recovering tetra alkyl lead from a reaction mass containing the same and unreacted lead-sodium alloy which comprises mixing the reaction mass with water, steam distilling the mixture, mixing with the distillation residue an acid reacting compound sufficient in amount to materially reduce the alkalinity of the mixture to a pH of between about 11 and 7.0 and then redistilling the mixture with steam.

3. The process of recovering tetra alkyl lead from a reaction mass containing the same and unreacted lead-sodium alloy which comprises mixing the reaction mass with water, steam distilling the mixture, mixing with the distillation residue an acid reacting compound sufficient in amount to materially reduce the alkalinity of

the mixture to a pH of between about 8 and 7.0 and then redistilling the mixture with steam.

4. The process of recovering tetra ethyl lead from a reaction mass containing the same and unreacted lead-sodium alloy which comprises mixing the reaction mass with water, steam distilling the mixture, mixing with the distillation residue an acid reacting compound sufficient in amount to materially reduce the alkalinity of the mixture to a pH of not lower than 7.0 and then redistilling the partially neutralized mixture with steam.

5. The process of recovering tetra ethyl lead from a reaction mass containing the same and unreacted lead-sodium alloy which comprises mixing the reaction mass with water, steam distilling the mixture, mixing with the distillation residue an acid reacting compound sufficient in amount to materially reduce the alkalinity of the mixture to a pH of between about 11 and 7.0 and then redistilling the mixture with steam.

6. The process of recovering tetra ethyl lead from a reaction mass containing the same and unreacted lead-sodium alloy which comprises mixing the reaction mass with water, steam distilling the mixture, mixing with the distillation residue an acid reaction compound sufficient in amount to materially reduce the alkalinity of the mixture to a pH of between about 8 and 7.0 and then redistilling the mixture with steam.

7. The process of recovering tetra ethyl lead from a reaction mass containing the same and unreacted lead-sodium alloy which comprises mixing the reaction mass with water, steam distilling the mixture, mixing with the distillation residue sulfuric acid sufficient in amount to materially reduce the alkalinity of the mixture to a pH of not lower than 7.0 and then redistilling the partially neutralized mixture with steam.

8. The process of recovering tetra ethyl lead from a reaction mass containing the same and unreacted lead-sodium alloy which comprises mixing the reaction mass with water, steam distilling the mixture, mixing with the distillation residue sulfuric acid sufficient in amount to materially reduce the alkalinity of the mixture to a pH of between about 11 and 7.0 and then redistilling the mixture with steam.

9. The process of recovering tetra ethyl lead from a reaction mass containing the same and unreacted lead-sodium alloy which comprises mixing the reaction mass with water, steam distilling the mixture, mixing with the distillation residue sulfuric acid sufficient in amount to materially reduce the alkalinity of the mixture to a pH of between about 8 and 7.0 and then redistilling the mixture with steam.

10. The process of recovering tetra ethyl lead from a reaction mass containing the same and unreacted lead-sodium alloy which comprises mixing the reaction mass with water, steam distilling the mixture, mixing with the distillation residue ammonium sulfate sufficient in amount to materially reduce the alkalinity of the mixture to a pH of between about 11 and 7.0 and then redistilling the mixture with steam.

11. The process of recovering tetra ethyl lead from a reaction mass containing the same and unreacted lead-sodium alloy which comprises mixing the reaction mass with water, steam distilling the mixture, mixing with the distillation residue a carboxylic acid sufficient in amount to materially reduce the alkalinity of the mixture to a pH of between about 11 and 7.0 and then redistilling the mixture with steam.

12. The process of recovering tetra ethyl lead from a reaction mass containing the same and unreacted lead-sodium alloy which comprises mixing the reaction mass with water, steam distilling the mixture, mixing with the distillation residue acetic acid sufficient in amount to materially reduce the alkalinity of the mixture to a pH of between about 11 and 7.0 and then redistilling the mixture with steam.

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