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PROCESS FOR STABILIZING OR DEACTIVATING SLUDGES, PRECIPITATES, AND RESIDUES OCCURRING OR USED IN THE MANUFACTURE OF TETRAALKYL LEADS

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This invention relates to a process for stabilizing or deactivating sludges, precipitates and residues occurring or used in the manufacture of tetraalkyl leads, and which normally tend to promote decomposition and ignition of the tetraalkyl leads that may be contained therein.

It is known that alkyl metal compounds in general are quite unstable and decompose readily, particularly in the presence of air or oxygen. It has also been found that these alkyl metal compounds are particularly unstable when adsorbed on materials which present a large surface area per unit volume such as silica gel, clays, alumina, earths, asbestos, charcoal, and materials of similar structure which materials appear to exert a catalytic effect in the decomposition of these alkyl metal compounds. Even tetraalkyl leads such as tetraethyl lead which is known to be somewhat more stable than some of the other alkyl metal compounds decomposes and often ignites in the presence of oxygen when small amounts are adsorbed on materials that offer extended surface areas, particularly when the masses containing the tetraethyl lead are exposed to temperatures somewhat higher than normal atmospheric temperatures. The tendency to oxidize and ignite, of course, varies with the substance with which the alkyl metal compound is incorporated, some materials apparently exerting a greater catalytic effect than others in promoting ignition of the alkyl lead compounds.

In the manufacture of tetraalkyl leads, such as tetraethyl lead, tetramethyl lead and the mixed ethyl-methyl lead compounds, sludges are formed from which it is difficult and, from a practical standpoint, impossible to entirely free from the alkyl lead compounds during the normal steam distillations or decantation operations. There is, therefore, carried through the process very finely divided lead and impurities such as bismuth compounds which, although present in very small amounts, finally are deposited as sludges in the pipes and tanks and other processing equipment, and these sludges which contain tetraethyl lead adsorbed therein when exposed to oxygen or air often ignite, thus presenting serious ignition and explosion hazards in the process.

Methods have been advanced for the removal of practically all the sludge forming materials from the tetraethyl lead after its distillation, such as by controlled blowing with air or oxygen with agitation, preferably under a layer of water, followed by separation of the precipitated sludge, as more particularly described in copending application Ser. No. 393,680. However, even in these cases the sludges which are deposited by the action of the oxidizing agent and which invariably contain tetraethyl lead, tend to ignite when exposed to air thus presenting serious ignition hazards, making it desirable that even these sludges should be deactivated during their formation or afterwards to permit of their removal and disposal in a safe manner.

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It is therefore an object of this invention to provide a process for stabilizing sludges, precipitates and residues occurring in the manufacture of tetraalkyl lead compounds whereby the ignition hazard presented by the lead alkyl compounds in contact with such catalytic surfaces is reduced or completely overcome.

It is a still further object of the invention to render inactive materials which tend to exert a catalytic effect in the decomposition of tetraalkyl leads in the presence of air thus permitting the safe use of such materials as filter aids in the manufacture of tetraalkyl lead.

I have found that sludges, precipitates and residues occurring or involved in the production of tetraalkyl leads which offer large surface areas per unit volume and which normally tend to exert catalytic effect and cause decomposition and ignition of the tetraalkyl lead which may be contained therein can be rendered inactive conveniently and economically by washing or otherwise treating them with solutions or dispersions of oil soluble copper or iron salts of organic carboxylic acids. These stabilizing or deactivating agents appear to be preferentially absorbed by the active materials, which materials retain their capacity to absorb the tetraalkyl lead, although they no longer have the property of inducing ignition of the tetraalkyl lead absorbed therein.

By the terms sludges, precipitates and residues I include those filter aids which may be employed in the production of the tetraalkyl leads and which offer a large surface area per unit volume and are known to accelerate decomposition of the tetraalkyl leads on exposure to air or oxygen such as clays, silica, earths, charcoal, etc. These filter aids are rendered inactive by treating them with copper or iron salts of organic carboxylic acids either before or after they are employed in the process. The effectiveness of these copper or iron salts in the deactivation of these active materials is not materially reduced by washing the deactivated materials with water or other solvents or by drying them down prior to use.

The copper or iron salts of organic carboxylic

acids, being oil soluble compounds, may be dissolved directly in the tetraalkyl lead before the sludge is precipitated by the method more particularly described in copending application Ser. No. 393,680. They may be added to the tetraalkyl lead after the sludge has been precipitated but before the tetraalkyl lead and sludge are separated; they may be added to a slurry of the tetraalkyl lead and sludge; or they may be dissolved in a suitable solvent and agitated with the separated sludge. These deactivators may be employed as a dispersion or a suspension in any type of solvent that may be desired for use in the treating of the tetraalkyl lead.

In general, the quantity of stabilizing agent required will be from about 1 to 10% based on the dry weight of the active material to be treated so that in the treatment of the sludges occurring in or to be precipitated from the crude tetraethyl lead in the usual methods of manufacture in which there are usually not more than two parts of precipitated sludge obtainable from the 1,000 parts of crude tetraethyl lead, it has been found that if 0.1 to 0.2 part of the stabilizing agents be employed per 1,000 parts of crude tetraethyl lead the sludges precipitated therefrom will be stabilized and when dried or heated will not cause ignition of the tetraethyl lead that may be contained therein. The amount of deactivator employed may, of course, be varied over a wide range. Good results have been obtained with concentrations as low as 0.05% of the deactivator based on the weight of the dry active material. While amounts as high as 100% based on the dry weight of the active material may be employed, the use of excessively large amounts over that actually required to deactivate the active material merely contributes unnecessarily to the cost of the process and serves no useful purpose.

In treating dry materials such as the filtered tetraethyl lead sludge, filter aids or the like, the quantity of stabilizing agent required may be dissolved in a suitable solvent. Good results have been obtained with solutions of the deactivator of concentrations as low as 0.05%. The upper limit of concentration will, of course, usually be determined by the solubility of the deactivator in the particular solvent employed. It is, of course, advantageous to employ a sufficient amount of solution to insure complete contact with all the material to be deactivated. If dispersions or suspensions of the deactivator are used, it will be found advisable to employ somewhat larger quantities and concentrations in order to insure adequate contact between the active material and the stabilizing agent within a reasonable time.

Where the sludges or precipitates settle out in the pipe lines or other processing equipment during the manufacture or purification of the tetraalkyl leads, they may be deactivated, to insure safety in their removal or during repair of the equipment, by pumping a solution of one of the deactivating materials through the apparatus for a sufficient period of time to insure complete contact with all the sludge to be deactivated, which is usually accomplished in from 15 to 30 minutes. Where a quantity of the sludge is obtained in cleaning out the equipment, it may be transferred to a suitable tank and agitated with a solution of the deactivator until complete deactivation is effected.

The filter aids may be washed with a solution of the deactivating agent prior to their use in the process. They may be employed either before or after drying, for it has been found that they do not again become active even after being dried, or by being washed by the solutions that are filtered therethrough.

The following examples are given to illustrate the invention. The parts used are by weight.

Example 1

About 4 parts of cupric oleate were dissolved in approximately 20,000 parts of crude tetraethyl lead. The sludge forming impurities were then precipitated by blowing with air as more particularly described in the copending application Ser. No. 393,680. After the precipitation was complete, the tetraethyl lead and sludge were agitated for 15 minutes and filtered.

A small portion of the filter cake was then tested for ignition activity by placing it on a filter paper, wetting it with a small quantity of tetraethyl lead and heating on a steam bath. No signs of ignition or of charring of the filter paper were noted even after 24 hours heating.

A sample of sludge which had been produced in a similar manner from the same batch of tetraethyl lead, except that the addition of copper oleate had been omitted, when tested for activity as outlined above, ignited shortly after the sample was placed on the steam bath.

Example 2

Approximately 1,000 parts of crude tetraethyl lead were placed in a suitable container provided with an agitator. About 100 parts of water were added, and the sludge was precipitated by air blowing and collected in the water layer as disclosed in the previously mentioned application Ser. No. 393,680.

After the precipitation treatment was complete, the clear tetraethyl lead was decanted from the water layer in which the precipitated impurities were suspended. One part of ferric naphthenate was added to the aqueous sludge suspension, and the mixture was vigorously agitated for 30 minutes. The mixture was filtered, and a portion of the precipitated sludge was tested for ignition activity as previously described. It was found to be inactive. A sample of sludge taken before the ferric naphthenate was added was similarly tested and found to promote ignition of tetraethyl lead.

As illustrated in the above examples, the stabilizing agent may be added directly to the tetraalkyl lead to effect deactivation of the sludge that may be precipitated by air blowing or by any other process, or the sludge may be collected and separated from the tetraalkyl lead and stabilized by treatment with a suspension or solution of the deactivating metal salts.

When 10 parts of an active sludge were treated with 50 parts of a solution containing 0.1 part of one of the following oil soluble salts of the carboxylic acids mentioned, complete deactivation of the sludge was effected so that when tested as described in Example 1 no ignition or charring was observed even after 72 hours of heating: cupric oleate, cupric naphthenate, ferric oleate, ferric stearate, cupric palmitate, ferric naphthenate, ferric palmitate, and the copper (cupric and cuprous) and the iron (ferric and ferrous) salts of stearic acid, 2-ethyl caproic acid, lauric acid, linoleic acid, hydroxy stearic acid, naphthyl stearic acid, ricinoleic acid, alkylated benzoic acids such as amyl benzoic acid, para dodecoxy benzoic acid, stearoyl benzoic acid, and mixtures of acids obtained by saponification of coconut oil, tallow and other glycerides, and abietic acid.

Where the untreated sludge employed in these tests was subjected to the same ignition test as described in Example 1, it ignited shortly after being placed on the steam bath.

As previously stated the invention may be employed to stabilize active filter aids which are to be used in tetraalkyl lead filtration. These materials may be washed in a solution of one of the deactivators and rendered suitable for tetraalkyl lead filtration. The following filter aids as well as a number of other materials of similar structure were wet with tetraethyl lead and placed on a steam bath as described in Example 1 above. All were found to initiate the ignition of tetraethyl lead. Ten parts of each of these materials were then agitated for several hours with 50 parts of a benzene solution of the copper and iron salts of the carboxylic acids of the concentrations given in the following table. After the agitation period the solutions were filtered and portions of the filter cakes were wet with tetraethyl lead and placed on a steam bath. Results of these tests were as given in the following table:

Material	Wash solution.	Steam bath test
Filter aid (clay)	None	Ignited.
Do	1% ferric stearate	No decomposition.
Filter aid (silica)	None	Ignited.
Do	0.2% ferric oleate	No decomposition.
Yellow lead oxide (N. F. VI).	None	Ignited.
Do	0.5% cuprous naphthenate.	No decomposition.
Bismuth subnitrate	None	Ignited.
Do	0.2% ferrous palmitate	No decomposition.
Bismuth oxide (from hydrolysis of $Bi(NO_3)_3$).	None	Ignited.
Do	0.5% cubric oleate	No decomposition.
Ferric oxide (anh.)	None	Ignited.
Do	0.2% cupric naphthenate.	No decomposition.
Activated Alumina	None	Ignited.
Do	0.2% cuprous palmitate	No decomposition.
Decolorizing charcoal	None	Ignited.
Do	0.2% ferric naphthenate.	No decomposition.

Example 3

Approximately 1,000 parts of crude tetraethyl lead and an equal weight of water were placed in a washer. Five parts of ferric stearate were then added and the sludge was precipitated and removed from the tetraethyl lead by the method disclosed in the copending application Ser. No. 393,680. After this operation was complete, the tetraethyl lead was removed by decantation, and the aqueous layer containing the sludge was filtered. A portion of the filter cake was then tested on the steam bath as described in Example 1. No decomposition or ignition of the tetraethyl lead was noted.

Example 4

As previously stated, sludges found in tetraethyl lead are also found in other lead alkyls which are manufactured from commercial lead. An example is the mixed tetramethyl-ethyl compounds of lead, formed when a mixture of methyl chloride and ethyl chloride is reacted with lead-sodium alloy. All examples in which tetraethyl lead is specified are equally workable with these mixed lead alkyls.

Approximately 8,000 parts of crude mixed tetramethyl-ethyl lead compounds (tetramethyl lead, trimethyl ethyl lead, dimethyl diethyl lead, methyl triethyl lead and tetraethyl lead) were

placed in a suitable tank or washer, and 2 parts of cuprous naphthenate were dissolved therein. The contents of the tank were aerated and agitated for two hours as disclosed in the copending application Ser. No. 393,680. After a settling period of a few minutes, the clear mixture of lead alkyls was decanted from the aqueous layer and the aqueous mixture was filtered. A portion of the filter cake was tested on the steam bath as described in Example 1, except that the filter cake (sludge) was wet with mixed lead alkyl compounds rather than with tetraethyl lead. No decomposition or ignition of the lead alkyls was noted. A similar experiment was carried out in which no stabilizing agent was added. This sludge ignited the mixed alkyls when the stability test was made.

A further use of this invention will be found in the storage of the crude tetraalkyl leads before they are desludged. These deactivating copper and iron salts may be dissolved directly in the tetraalkyl lead so that any sludge which precipitates out on standing will be rendered inactive by contact with the deactivating agent.

In testing the activity of the sludges before or after treatment with the deactivating agents, it will be noted that tetraethyl or other alkyl lead was added to the residues. This was to make sure there was sufficient tetraalkyl lead present to ignite under the conditions employed, if the sludge was not fully inactivated, for in some instances, it is possible that the amount of alkyl lead may be reduced to such a small amount that ignition might not be noted. While the elimination of the alkyl lead from the residues to such an extent does not ordinarily take place, the tests were made under conditions favoring ignition provided the sludge or filter aid was active.

This invention makes possible the deactivation of the ignitable sludges and residues occurring in the manufacture of tetraalkyl lead compounds and is of particular value in eliminating fire and explosion hazards involved in the removal and disposal of such sludges from the process and in overcoming the potential fire hazard arising from the collection of such sludges and precipitates which accumulate in various places in the processing equipment and which when exposed to air often ignite with considerable damage. The invention also permits the use of filter aids which, unless rendered inactive, tend to cause ignition of any absorbed tetraethyl lead when they are exposed to the air. Any other absorbent materials which for any reason may become saturated with tetraethyl lead in or about the plant in which it is being manufactured may be rendered inactive by washing or otherwise treating with stabilizers of the type described so that potential fire hazards may be removed as far as possible. Lagging on pipe which due to leaks may become saturated with tetraethyl lead and which have been known to cause its ignition can be inactivated by treating such lagging with the deactivating agents.

I claim:

1. The process for inhibiting the spontaneous ignition of tetraalkyl lead compounds adsorbed on sludges which are precipitated from crude tetraalkyl lead compounds and which sludges normally tend to cause spontaneous ignition of the tetraalkyl lead compounds adsorbed thereon when exposed to oxygen, which comprises incorporating with such sludges a compound of the group consisting of oil soluble copper salts of carboxylic acids and oil soluble iron salts of carboxylic acids.

2. The process for inhibiting the spontaneous ignition of tetraethyl lead adsorbed on sludges which are precipitated from crude tetraethyl lead and which sludges normally tend to cause spontaneous ignition of the tetraethyl lead adsorbed thereon when exposed to oxygen, which comprises incorporating with such sludges a compound of the group consisting of oil soluble copper salts of carboxylic acids and oil soluble iron salts of carboxylic acids.

3. The process for inhibiting the spontaneous ignition of tetraalkyl lead compounds adsorbed on solid materials which present a large surface area per unit volume and which normally tend to cause spontaneous ignition of the tetraalkyl lead compounds adsorbed thereon when exposed to oxygen, which comprises washing such materials with a solution of a compound of the group consisting of oil soluble copper salts of carboxylic acids and oil soluble iron salts of carboxylic acids.

4. The process for inhibiting the spontaneous ignition of tetraethyl lead adsorbed on sludges which are precipitated from crude tetraethyl lead and which sludges normally tend to cause spontaneous ignition of the tetraethyl lead adsorbed thereon when exposed to oxygen, which comprises washing such sludges with a solution of a compound of the group consisting of oil soluble copper salts of carboxylic acids and oil soluble iron salts of carboxylic acids.

5. The process for inhibiting the spontaneous

ignition of tetraethyl lead adsorbed on solid materials which present a large surface area per unit volume and which normally tend to cause spontaneous ignition of the tetraethyl lead adsorbed thereon when exposed to oxygen, which comprises incorporating with such materials an oil soluble copper naphthenate.

6. The process for inhibiting the spontaneous ignition of tetraethyl lead adsorbed on sludges which are precipitated from crude tetraethyl lead and which sludges normally tend to cause spontaneous ignition of the tetraethyl lead adsorbed thereon when exposed to oxygen, which comprises incorporating with such sludges an oil soluble copper naphthenate.

7. The process for inhibiting the spontaneous ignition of tetraethyl lead adsorbed on sludges which are precipitated from crude tetraethyl lead and which sludges normally tend to cause spontaneous ignition of the tetraethyl lead adsorbed thereon when exposed to oxygen, which comprises incorporating with such sludges an oil soluble copper oleate.

8. The process for inhibiting the spontaneous ignition of tetraethyl lead adsorbed on sludges which are precipitated from crude tetraethyl lead and which sludges normally tend to cause spontaneous ignition of the tetraethyl lead adsorbed thereon when exposed to oxygen, which comprises incorporating with such sludges an oil soluble iron stearate.

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