Patented Dec. 8, 1931 1,835,140

UNITED STATES PATENT OFFICE

WILLIAM S. CALCOTT, OF PENNS GROVE, AND ALFRED E. PARMELEE, OF CARNEYS POINT, NEW JERSEY, ASSIGNORS TO E. I. DU PONT DE NEMOURS & COMPANY, OF WILMINGTON, DELAWARE, A CORPORATION OF DELAWARE

STABILIZATION OF TETRA ALKYL LEAD AND COMPOSITIONS CONTAINING THE SAME

No Drawing. Application filed October 31, 1929. Serial No. 403,907.

This invention relates to the stabilization of tetra alkyl lead, unmixed with anything but its normal impurities, and to the stabilization of tetra ethyl lead mixed with such materials as hydrocarbons and halogen derivatives of hydrocarbons. More particularly our invention relates to the stabilization of tetra ethyl lead and mixtures containing tetra ethyl lead by the incorporation therewith of small amounts of di aryl amines or of certain derivatives of di aryl amines.

Ordinary commercial tetra alkyl lead, and particularly tetra ethyl lead, decomposes slowly on standing, and this decomposition is accelerated when these compounds contain in addition such organic substances as halogen derivatives of hydrocarbons.

We have discovered that this decomposition can be very materially retarded or prevented by the introduction of di aryl amines or derivatives of diarylamines such, for example, as the mono- and di-hydroxy, alkoxy, and amino substituted diaryl amines. The class of compounds which we have found to be effective for the stabilization of tetra ethyl lead may be represented by the general formula $X_1—R_1—NH—R_2—X_2$, wherein R_1 and R_2 are aromatic hydrocarbon nuclei which may be alike or different and X_1 and X_2 are hydroxy, alkoxy, amino, or hydrogen.

In order to disclose the invention in detail, the following examples of actual embodiments thereof are presented. It is to be understood, however, that these examples are furnished purely for purposes of illustration and that it is not the intention that the invention is to be limited to the paricular reagents, proportions or other conditions therein specified.

Example 1

Fifty grams of tetra ethyl lead, 45 grams of ethylene dibromide, and 5 grams of mono chlor naphthalene are combined. To this composition is added phenyl-a-naphthylamine in amounts up to one gram.

Example 2

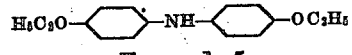
To 100 grams of tetra ethyl lead is added, with stirring, 0.1 gram of diphenylamine.

Example 3

To 100 grams of tetra methyl lead is added, with stirring, 0.05 gram of p-hydroxy diphenylamine.

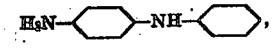
Example 4

One hundred grams tetraphenyl lead are mixed with 90 grams ethylene dibromide and 0.2 gram diethoxy diphenylamine,



Example 5

Fifty grams of tetra ethyl lead, 45 grams of ethylene dibromide, and 5 grams of mono chlor naphthalene are combined. To this composition is added p-amino diphenylamine,



in amounts up to one gram.

Example 6

Fifty grams of tetra ethyl lead, 45 grams of ethylene dibromide, and 5 grams of mono chlor naphthalene are combined. To this composition is added 2:4 diamino 4' hydroxy diphenylamine in amounts up to one gram.

The foregoing compositions will be found remarkably stable against decomposition as evidenced by the fact that they remain free from insoluble matter for long periods of time or the formation of any insoluble precipitate will be greatly reduced. For example, with 0.5% phenyl-a-naphthylamine samples of tetra ethyl lead have remained stable and free from sediment for eight months, which otherwise would decompose giving rise to a substantial precipitate in three to four days or less.

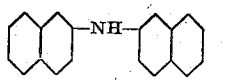
While phenyl-alpha-naphthylamine is our preferred compound for stabilizing these lead compounds, the foregoing compounds have been found satisfactory.

There are also a large number of compounds which may be used effectively for the purpose herein described, and these may be obtained by the substitution of various groups such as hydroxy, alkoxy, or amino in the aryl nuclei of the di aryl amines may take place

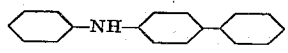
singly, that is substituting only one group, or doubly introducing two groups which may be alike or different as, for example, in di-OH diphenylamine and in p-amino-p'-OH diphenylamine.

Phenyl-b-naphthylamine,

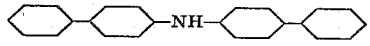
b-b' dinaphthylamine,



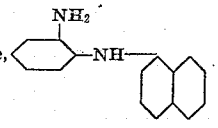
Phenyl-biphenylamine,



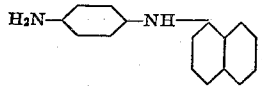
Di biphenylamine,



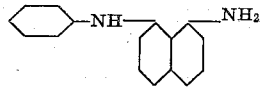
o-amino phenyl-b-naphthylamine,



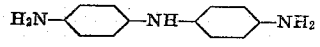
p-amino phenyl-a-naphthylamine,



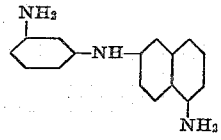
1-phenylamino-8-amino naphthalene,



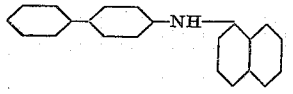
pp'-diamino diphenylamine,



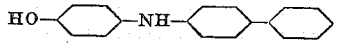
m-amino phenyl-a-5-amino naphthylamine,



Biphenyl-a-naphthylamine,



p-hydroxy phenylbiphenylamine,



Of these compounds, however, phenyl-alpha-naphthylamine represents our preferred embodiment.

It will be understood, of course, that either tetra ethyl lead or tetra methyl lead may be included in any one of the foregoing illustrative examples. We have found that these solutions so prepared will remain stable indefinitely under the conditions ordinarily employed for the storage of tetra alkyl lead compounds and the compositions containing these compounds.

As many apparently widely different embodiments of this invention may be made without departing from the spirit thereof, it is to be understood that we do not limit ourselves to the foregoing examples or descriptions except as indicated in the following patent claims.

We claim:

1. A composition comprising tetra alkyl lead having incorporated therewith a stabilizing compound having the general formula

$$X_1—R_1—NH—R_2—X_2$$

wherein R_1 and R_2 are aromatic hydrocarbon nuclei which may be alike or different, and X_1 and X_2 are hydroxy, alkoxy, amino groups, or hydrogen.

2. The composition of claim 1 wherein, in the formula of the stabilizing compound, at least one of the R_1 and R_2 represents a phenyl group.

3. The composition of claim 1 wherein, in the formula of the stabilizing compounds, R_1 and R_2 both represent phenyl groups.

4. The composition of claim 1 wherein, in the formula of the stabilizing compound, X_1 and X_2 both represent OH.

5. The composition of claim 1 wherein, in the formula of the stabilizing compound, at least one of R_1 and R_2 represents a phenyl group and X_1 represents OH.

6. A composition comprising tetra alkyl lead having incorporated therewith phenyl-alpha-naphthylamine.

7. The invention of claim 6 in which the tetra alkyl lead is tetra ethyl lead.

9. A composition comprising tetra alkyl lead, hydrocarbons and halogen derivatives of hydrocarbons, and a stabilizing compound having the general formula

$$X_1—R_1—NH—R_2—X_2$$

wherein R_1 and R_2 are aromatic hydrocarbon nuclei which may be alike or different and X_1 and X_2 are hydroxy, alkoxy, amino groups or hydrogen.

9. The composition of claim 8 wherein, in the formula of the stabilizing compound, at least one of the R_1 and R_2 represents a phenyl group.

10. The composition of claim 8 wherein, in the formula of the stabilizing compound, R_1 and R_2 both represent phenyl groups.

11. The composition of claim 8 wherein, in the formula of the stabilizing compound, X_1 and X_2 both represent OH.

12. The composition of claim 8 wherein, in the formula of the stabilizing compound, at least one of R_1 and R_2 represents a phenyl group and X_1 represents OH.

13. A composition comprising tetra alkyl lead, hydrocarbons and halogen derivatives of hydrocarbons, having incorporated therewith phenyl-alpha-naphthylamine.

14. The invention of claim 13 in which the tetra alkyl lead is tetra ethyl lead.

15. A composition comprising tetra alkyl lead having incorporated therewith a stabilizing compound comprising a di-aryl-amine.

16. A composition comprising tetra alkyl lead, hydrocarbons, and halogen derivatives of hydrocarbons, having incorporated therewith a stabilizing compound comprising a di-arylamine.

In testimony whereof we affix our signatures.

WILLIAM S. CALCOTT.
ALFRED E. PARMELLE.