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UNITED STATES PATENT OFFICE.

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PROCESS OF PREPARING METALLIC SALTS OF DITHIOCARBAMIC ACID.

No Drawing. Application filed August 9, 1921. Serial No. 491,042.

To all whom it may concern:

Be it known that I, YASUJURO NIKAIDO, a citizen of Japan, and a resident of Bay City, in the county of Bay and State of Michigan, U. S. A., have made a new and useful invention in Processes of Preparing Metallic Salts of Dithiocarbamic Acid, of which the following is a specification.

My invention relates to the production of metallic salts of alkylated dithiocarbamic acid and more particularly to the methylated compounds.

In United States Patent 1,465,677 to Molony and Nikaido August 21, 1923 there is described amino-ammonium salts of dithiocarbamic acid, such as the amino-ammonium salt of monomethyl and dimethyl dithiocarbamic acid, wherein beet sugar residue is utilized as one of the reacting materials. These salts, characterized by a very disagreeable odor, are exceedingly unstable, affording a comparatively small yield, about one per cent of the weight of the beet sugar residue used.

I have found that a stable compound, affording a yield of approximately six per cent by weight of the beet sugar residue used may be produced if the dithiocarbamic compounds are in the form of metallic salts. The production of the metallic salts of dithiocarbamic acid utilizing as one of the reacting materials the impure gases derived from the distillation of beet sugar residue involves several difficulties. The present invention is designed to overcome the same.

I have found that the amino-ammonium salts of dithiocarbamic acid derived from the treatment of beet sugar residue with carbon bisulfid contain ammonium sulfid, ammonium hydrate, ammonium sulphocyanate and possibly other undesirable ammonium compounds. If a zinc salt is added directly to the amino-ammonium salts of dithiocarbamic acid a considerable amount of zinc sulfid and hydroxid are formed which render the resulting salt of dithiocarbamic acid exceedingly impure. I have ascertained that a pure salt may be obtained by acidifying the dithiocarbamic acid solution with a weak acid before the addition of the zinc salt. Strong acids, such as mineral acids, cannot be used, since they decompose the amino-ammonium salts of dithiocarbamic acid. Acetic acid has been found satisfactory.

I have also found that unless the dithiocarbamic acid solution is considerably diluted the precipitate formed upon the addition of the zinc salt will be lumpy causing considerable loss in filtration. A diluted solution gives, upon the addition of metallic salt, a granular precipitate which is easily filtered. A 5% solution has given good results.

After the amino-ammonium salt-solution of dithiocarbamic acid has been diluted and acidified with a weak acid, a solution of a zinc salt, preferably zinc sulfate, is added thereto. A 10% solution of the zinc sulfate is preferred, this dilution giving a precipitate admitting of efficient filtration. The zinc salts formed are separated from the mother-liquor by centrifuging, and are thereafter dried in a current of warm dry air. Theoretically one half of the amine in the amino salt of dithiocarbamic acid, for example the amino-ammonium salt of dimethyl dithiocarbamic acid, goes into solution as hydrosulfate of dimethylamine, according to the following equation, and is found in the filtrate:

$$2\,C{\leq}\begin{matrix}N(CH_3)_2\\ SNH_2(CH_3)_2\end{matrix}{=}S \;+\; ZnSO_4 \;=\; Zn\left(C{\leq}\begin{matrix}N(CH_3)_2\\ S\end{matrix}{=}S\right)_2 \;+\; \left(NH(CH_3)_2\right)_2 H_2SO_4$$

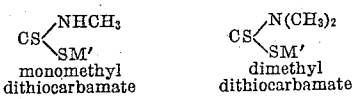
The filtrate resulting from the precipitation of the zinc salts contains a considerable amount of amine-hydrosulfate. The amines may be recovered from the filtrate by evaporating the same and thereafter distilling the evaporated mass in a still in the presence of an amine librating-medium, for example finely-divided lime. The amines are then passed into carbon bisulfid forming the amino-salts of dithiocarbamic acid. The recovery of the amines from the zinc filtrate materially increases the yield of the zinc dithiocarbamic compound.

An analysis of the precipitate formed during one of the runs gave the following:

Monomethyl dithiocarbamate of zinc 16.98%
Dimethyl dithiocarbamate of zine 75.19%
Balance impurities and moisture.

The metallic salts produced are a mono-

methyl dithiocarbamate and dimethyl dithiocarbamate of the metal, or a mixture of the two. These compounds have the following formulas:



monomethyl dithiocarbamate — dimethyl dithiocarbamate

Other metallic salts of these acids, such as iron, mercury and lead, may be made in a similar manner.

I claim:

1. The process of producing stable metallic salts of alkyl dithiocarbamic acid comprising passing the distillation-product formed by the destructive distillation of beet sugar residue into carbon bisulfid, separating therefrom a solution of the amino-ammonium salts of dithiocarbamic acid, acidifying the solution with a weak acid, adding a metal salt thereto, and recovering therefrom the metallic salts of dithiocarbamic acid.

2. The process of producing stable zinc salts of alkyl dithiocarbamic acid comprising passing the distillation-product formed by the destructive distillation of beet sugar residue into carbon bisulfid, separating therefrom a solution of the amino-ammonium salts of dithiocarbamic acid, acidifying the solution with a weak acid, adding a zinc salt thereto, and recovering therefrom the zinc salts of alkyl dithiocarbamic acid.

3. The process of producing stable zinc salts of methylated dithiocarbamic acid comprising passing the distillation-product formed by the destructive distillation of beet sugar residue into carbon bisulfid, separating therefrom a solution of the amino-ammonium salts of dithiocarbamic acid, acidifying the solution with a weak acid, adding a zinc salt thereto, and recovering therefrom the zinc salts of methylated dithiocarbamic.

4. The process of producing stable metallic salts of alkyl dithiocarbamic compounds comprising passing the distillation-product formed by the destructive distillation of beet sugar residue into carbon bisulfid, separating therefrom a solution of the amino-ammonium salts of dithiocarbamic acid, diluting the solution, acidifving the solution with a weak acid, adding a metal salt thereto, and recovering therefrom the metallic salts of dithiocarbamic acid.

5. The process of producing stable metallic salts of alkyl dithiocarbamic compounds comprising passing the distillation-product formed by the destructive distillation of beet sugar residue into carbon bisulfid, separating therefrom a solution of the amino-ammonium salts of dithiocarbamic acid, adding a metallic salt thereto to precipitate the metallic salts of dithiocarbamic acid, separating the precipitate from the filtrate, recovering the amines from the latter, passing the same into carbon bisulfid for the formation of additional amino salts of dithiocarbamic acid, treating the latter with a metallic salt, and recovering the metallic salts of dithiocarbamic acid.

6. The process of producing stable metallic salts of alkyl dithiocarbamic acid comprising passing the distillation-product formed by the destructive distillation of beet sugar residue into carbon bisulfid, separating therefrom a solution of the amino-ammonium salts of dithiocarbamic acid, acidifying the solution with a weak acid, adding a metal salt thereto to precipitate the metallic salts of dithiocarbamic acid, separating the precipitate from the filtrate and recovering the amines present in the filtrate for further use in the process.

7. The process of producing stable metallic salts of alkyl dithiocarbamic acid comprising passing the distillation-product formed by the destructive distillation of beet sugar residue into carbon disulfid, separating therefrom a solution of the amino-ammonium salts of dithiocarbamic acid, adding a metal salt thereto to precepitate the metallic salts of dithiocarbamic acid, separating the precipitate from the filtrate and recovering the amines present in the filtrate for further use in the process.

In testimony whereof, I have hereunto subscribed my name this 20th day of July, 1921.

YASUJURO NIKAIDO.

Witnesses:
WARREN E. CARTER,
EDWIN O. LIST.