UNITED STATES PATENT OFFICE

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METHOD OF MANUFACTURING TETRA-ALKYLATED THIURAMDISULPHIDES

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When a di-alkyl dithiocarbamate is oxidized to a thiuramdisulphide by treatment with a halogen or other oxidizing agent, two molecules of amine are simultaneously liberated. If the reaction be carried out with pure materials, the liberated amine will naturally be a secondary amine. If the reaction is carried out by treating a mixture of primary, secondary and tertiary amines with carbon disulphide, the amine liberated upon oxidation may be composed partially of secondary amine but where considerable tertiary amine is present, the tertiary amine will remain as free amine. When oxidizing agents other than halogenes are used, the amine or amines liberated or not reacted with are less liable to oxidation. If the oxidizing agent be introduced very slowly, the extent of oxidation of the amines may be reduced, but even so there is still a considerable loss of valuable raw materials.

The present invention relates primarily to methods of protecting from oxidation the amines liberated in the course of the oxidation of dithiocarbamates to disulphides.

Another object of the invention is to provide an improved method for manufacturing tetra-alkylated thiuramdisulphides. A further object is to oxidize dithiocarbamates under such conditions that free amines in the reaction mixture are not destroyed. Another object of the invention is to provide an improved and economical method for manufacturing tetraalkylated thiuramdisulphides by carrying out the oxidation of suitable dithiocarbamates with an oxidizing agent in the presence of a reagent adapted to form a useful raw material with the amines liberated during, or not entering, the reaction of oxidation. Another object is to carry out the oxidation of suitable dithiocarbamates to corresponding thiuramdisulphides with a non-halogen oxidizing agent in the presence of an inorganic acid.

With a preferred method in mind, but without desiring to place undue limitations upon the scope of the invention beyond what may be required by the prior art, the invention consists in treating a secondary amine or mixture of amines containing secondary amine with carbon bisulphide to form the corresponding dithiocarbamate, oxidizing the dithiocarbamate with a non-halogen oxidizing agent in the presence of a reagent adapted to protect the liberated amine from oxidation, and continuing the several reactions until substantially all of the secondary amine has been converted into thiuramdisulphide. More specifically, the invention consists in carrying out the oxidation of the dithiocarbamate of a secondary amine to a thiuramdisulphide by means of hydrogen peroxide in the presence of sulphuric acid. The invention also includes carrying out such oxidation process in the presence of an excess of carbon disulphide, or by the addition of carbon bisulphide in such a manner as to cause substantially all of the secondary amine present to become converted into tetra alkylated thiuramdisulphide.

The salts of amines, particularly the amine salts of strong acids, are much less susceptible to oxidation than the free amines themselves. The present invention therefore aims to prepare such amine salts during the course of the reaction, as the amines are liberated, and thereby protect the amines against oxidation and loss, both of amines and of oxidizing agent. When halogen oxidizing agents are used, this is accomplished automatically, for the halogen in the presence of water gives rise to a halogen acid. However, the halogen oxidizing agents are expensive, cause undesirable side reactions, and have other disadvantages. Hydrogen peroxide is a satisfactory oxidizing agent, but does not automatically neutralize and thus protect the amines which it liberates during the oxidation of a dithiocarbamate into a thiuramdisulphide. If an equivalent amount of a suitable acid, such as hydrochloric acid or sul-
phric, be mixed with the hydrogen peroxide prior to its usage in the oxidation reaction, the acid automatically neutralizes the amines liberated or tertiary amine which does not enter the reaction, and thus accomplishes the protection and preservation of the amine, and at the same time avoids an undesirable wastage of oxidizing agent.

These reactions may be indicated as follows:

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\begin{align*}
NR_1 + H_2O + \text{HNO}_3 & \rightarrow 2RNI + H_2O \\
S + H_2O \rightarrow SO_2 + H_2O \\
S + H_2O + CS & \rightarrow 2RNI + CS + H_2O \\
(RNH)_2H_2SO_4 + H_2O & \rightarrow CO_3 + (R_2NH)_2H_2SO_4 + H_2O \\
(RNH)_2H_2SO_4 + 2NaOH & \rightarrow Na_2SO_4 + 2H_2O + 2RNH
\end{align*}
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The oxidizing agent is most conveniently prepared by diluting 98% sulphuric acid to a convenient strength such as 10–30% and cooling thoroughly before adding hydrogen peroxide thereto. This avoids the rise of temperature which would occur were the acid added to the peroxide, or the peroxide added to the concentrated acid.

As an illustration of the invention as applied to substantially pure dimethyl amine, the following is given: A water solution containing 180 lbs. of dimethyl amine is caused to react with 152 lbs. of carbon disulphide. The alkyl dithiocarbamate thus formed is then oxidized to tetramethylthiuram disulphide by adding with stirring and cooling, 453 lbs. of 73% hydrogen peroxide to which has been added 103 lbs. of 98% sulphuric acid with suitable dilution as indicated above. The tetramethylthiuram disulphide formed by the oxidation may then be filtered out, washed and dried. Approximately ½ of the dimethylamine appears as tetramethylthiuram disulphide. But the remainder of the amine, which is liberated during the oxidation reaction, has become automatically combined with the sulphuric acid to form dimethylamine sulphate. This dimethylamine sulphate remains in the filtrate and is recoverable. If desired the filtrate containing the 90 lbs. of dimethylamine as sulphate may be treated with 85 lbs. of sodium hydroxide or the equivalent amount of another alkali and liberated as the free amine. The free amine may be distilled off and absorbed in water and used again. Another convenient method of handling the dimethylamine sulphate is to free it by treatment with an alkali hydroxide and cause the free amine to react with additional carbon bisulphide to form dithiocarbamate, and repeating the oxidation as set forth in the above example. This may be continued until practically all of the dimethylamine has been converted into tetramethylthiuramdisulphide. Towards the latter stages tertiary amine or another base may be introduced.

While dimethylamine has been given as an example, it is of course understood that other secondary amines may be employed with equal facility. The invention may also be practiced upon a mixture of primary, secondary and tertiary amines or of primary and secondary amines or of secondary and tertiary amines or secondary amines and bases in solution which are not affected by the carbon disulphide or the oxidation reactions. The claims are understood as comprehending secondary amine or a mixture containing secondary amine.

As an example of carrying out the invention with a mixture of amines, the following may be given: A water solution of dimethylamine, trimethylamine and methylamine, containing in total 19.3 lbs. of nitrogen, may be treated with 52.4 lbs. of carbon bisulphide. The primary and secondary amines are converted into the corresponding dithiocarbamates while the tertiary amine is not changed. To the reaction mixture, with stirring and cooling, 156 lbs. of a 7.5% solution of hydrogen peroxide containing 54.6 lbs. of 98% sulphuric acid are added. The secondary amine is converted into the corresponding tetraalkylated thiuramdisulphide, the primary amine into the corresponding mustard oil, and the tertiary amine remains in solution as sulphate. The thiuramdisulphide is then filtered out, freed from the mustard oil, washed and dried.

The invention may also be carried out by treating dimethylamine or other secondary amine with an excess of carbon bisulphide, either by starting with an excess of the carbon bisulphide, but preferably adding the necessary excess after the oxidation. A water solution containing 80 lbs. of dimethyl amine may be treated with 76 lbs. of carbon bisulphide. The amine is converted into the corresponding dithiocarbamate which is then oxidized by treatment with 453 lbs. of a 7.5% solution of hydrogen peroxide, the latter being run in slowly with stirring and cooling. At the same time an additional 76 lbs. of carbon bisulphide may be run in at such rate.
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that the total amount of carbon bisulphide is added in approximately the same time as that required for the addition of the total amount of hydrogen peroxide. The tetramethyl-thiuramdisulphide thus formed may be filtered out, washed and dried. The simultaneous formation of dithiocarbamate from the dimethylamine liberated during the oxidation reaction, and the oxidation of the dithiocarbamate to the corresponding tetramethyl-thiuramdisulphide may be continued until approximately all of the dimethyl amine has been converted.

Having thus described our invention what we claim and desire to protect by Letters Patent is:

1. A process for making tetra alkylated thiuramdisulphides which comprises treating a secondary amine with an excess of carbon disulphide, oxidizing the dithiocarbamate thus formed to a thiuramdisulphide and causing the liberated secondary amine to react with the excess carbon disulphide to form additional dithiocarbamate, oxidizing the dithiocarbamate as it forms into further thiuramdisulphide and recovering the thiuramdisulphide from the reaction mixture.

2. A process for making tetramethylthiuramdisulphide which comprises treating dimethylamine with an excess of carbon disulphide, oxidizing the alkyl dithiocarbamate thus formed to tetramethylthiuramdisulphide and continuously causing the liberated dimethylamine to be converted into additional alkyl dithiocarbamate by reaction with the excess carbon disulphide and then oxidized to tetramethylthiuramdisulphide until substantially all the dimethylamine has been converted, and recovering tetramethylthiuramdisulphide from the reaction mixture.

3. A process for making tetramethylthiuramdisulphide which comprises treating dimethylamine with carbon disulphide, oxidizing the alkyl dithiocarbamate thus formed to tetramethylthiuramdisulphide with hydrogen peroxide and simultaneously causing the liberated dimethylamine to be converted into additional alkyl dithiocarbamate by the addition of excess carbon disulphide and oxidized to tetramethylthiuramdisulphide until substantially all the dimethylamine has been converted, and recovering tetramethylthiuramdisulphide from the reaction mixture.

Signed at New York, county of New York, and State of New York, this 31st day of July, 1925.

HAROLD S. ADAMS.

Signed at Naugatuck, county of New Haven, State of Connecticut, this 30th day of July, 1925.

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