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HYDRAZINE

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This invention relates generally to hydrazine and more particularly to a method for stabilizing hydrazine and aqueous solutions thereof.

It has been observed heretofore that atmospheric oxygen causes the decomposition of hydrazine and that this decomposition is due to autoxidation. It has also been known that copper accelerates the autoxidation of hydrazine exposed to air and consequently, containers and apparatus made from copper or alloys thereof have not been entirely suitable heretofore for utilization in the manufacture, transportation, etc. of hydrazine.

It is an object of this invention to provide a method for preventing the acceleration of the decomposition of hydrazine by a metal, such as copper, in contact therewith. Another object of the invention is to provide a method for retarding the dissolution of copper in hydrazine and aqueous solutions thereof and thus to preclude copper from accelerating the autoxidation of hydrazine. Still another object of the invention is to provide a method for retarding or substantially preventing the autoxidation of hydrazine which is in contact with an accelerating agent such as copper. A further object of the invention is to provide hydrazine solutions stabilized against autoxidation of hydrazine. A more specific object of the invention is to provide a method for preventing hydrazine from becoming contaminated with copper.

In accordance with this invention, the foregoing objects and others which will become apparent from the following description are accomplished, generally speaking, by dissolving an organic sulfide such as tetramethyl thiuram monosulfide, tetramethyl thiuram disulfide, 2,2 dibenzothiazyl sulfide or mixtures thereof in hydrazine or aqueous solutions thereof. It has been found in accordance with this invention that the dissolution of copper in hydrazine or in aqueous solutions thereof is retarded or substantially repressed if the solution contains a solute of any one of the foregoing organic inhibitors or mixtures thereof. It also has been found that the copper is in this way precluded from accelerating the autoxidation of the hydrazine. The effectiveness of tetramethyl thiuram disulfide, and 2,2 dibenzothiazyl sulfide or mixtures thereof is such that the autoxidation of hydrazine is inhibited even in the presence of a known accelerating agent such as chloride or other halide ion. Tetramethyl thiuram monosulfide, tetramethyl thiuram disulfide, and 2,2 dibenzothiazyl sulfide are not only effective as a repressent for the dissolution of copper or copper compounds in hydrazine but also function effectively in preventing copper present as a solute in the hydrazine before the inhibitor is added from accelerating the autoxidation of hydrazine. Thus, although it is preferred to prevent hydrazine from dissolving any copper or copper compound in contact therewith, the invention also provides a method for decelerating the rate of autoxidation of hydrazine if copper is already present as a solute. As little as 0.001 molar concentration of tetramethyl thiuram monosulfide, tetramethyl thiuram disulfide, and 2,2 dibenzothiazyl sulfide is ordinarily sufficient to prevent copper from dissolving

in hydrazine and to prevent autoxidation of the hydrazine. There is seldom any advantage in having a concentration of more than about 0.01 molar of any one or a combination of the inhibitors provided by the invention, although for some purposes greater concentrations are not usually objectionable.

In one embodiment of the invention about 0.001 mole tetramethyl thiuram monosulfide was dissolved in an aqueous solution of about 54.4 per cent by weight hydrazine and about 0.0005 mole sodium chloride. This solution was prepared in a chemically clean glass container and the volume of the solution was about one-third the volume of the container. A copper rod of such length that it extended throughout the height of the solution and into the air above the liquid was placed in the container. The container was tightly closed and was permitted to stand at prevailing room temperatures of about 68 to about 90° F. for seven months. At the end of this period of time the hydrazine content of the solution was about 53.7 per cent.

In a second embodiment conducted with a similar aqueous solution of hydrazine and sodium chloride and under similar conditions but with tetramethyl thiuram disulfide in a concentration of about 0.001 mole as the inhibitor, the solution after the seven months storage period contained about 52.6 per cent hydrazine.

In the third embodiment conducted with a similar hydrazine-sodium chloride solution and under conditions similar to those in the foregoing embodiments but with about 0.001 mole 2,2 dibenzothiazyl dissolved therein as the inhibitor, the aqueous solution contained about 52.8 per cent by weight hydrazine at the end of the seven months storage. This solution as well as the two utilized in the foregoing embodiments contained less copper than could be measured by the best available analytical methods at the end of seven months.

In contrast, an aqueous hydrazine solution not containing one of the inhibitors of the invention and having metallic copper or copper alloy in contact therewith rapidly decomposes with the formation of a blue color indicating that the hydrazine has been converted into nitrogen and ammonia and eventually into cupric ammoniate. In one test, about 88 per cent of the hydrazine originally present in an aqueous solution had been lost by decomposition after about two months storage at room temperatures and with metallic copper suspended therein. With certain concentrations of hydrazine, mirror deposits of copper are produced on the walls of the container while at other concentrations of hydrazine, metallic copper or derivatives thereof may be precipitated in colloidal form.

In each of the foregoing examples an aqueous solution containing about 54.4 per cent hydrazine was utilized for convenience but it has been found that each of the inhibitors provided by this invention is also effective in preventing copper from dissolving in hydrazine solutions of other concentrations. In fact, each of these inhibitors or mixtures thereof will retard or substantially prevent the dissolution of copper in very dilute solutions of hydrazine containing less than 5 per cent thereof as well as in the more concentrated solutions of hydrazine and substantially anhydrous hydrazine. Hence, "hydrazine" as utilized in the appended claims is intended to be inclusive of aqueous solutions of hydrazine as well as substantially anhydrous hydrazine.

No definite explanation of the phenomena involved in the retardation of the dissolution of copper by a hydrazine solution containing one of the inhibitors provided by this invention is presently available. However, one theory which has been suggested as an explanation of the phenomena is that the inhibitor forms some compound with the copper ions present in the surface of the metal which compound forms a protective film over the surface of the

metal and prevents the hydrazine from contacting other copper ions.

In the foregoing examples ambient temperatures were used for convenience but the compounds of the class provided by this invention are also effective in retarding the dissolution of copper in hydrazine solutions at other temperatures, either higher or lower. Furthermore, as pointed out hereinbefore, the inhibitors provided by this invention are also effective in preventing dissolved copper from accelerating the autoxidation of hydrazine although it is preferred to prevent the dissolution of the copper by adding the inhibitor before the solution comes into contact with any metal or compound containing copper.

Embodiments of the invention have been described in detail in the foregoing for the purpose of clarification only and many variations will occur to those skilled in the art and can be made therein without departing from the spirit of the invention or the scope thereof except as limited by the claims.

What is claimed and desired to secure by Letters Patent is:

1. Hydrazine containing an organic sulfide selected from the group consisting of tetramethyl thiuram monosulfide, tetramethyl thiuram disulfide, 2,2 dibenzothiazyl sulfide and mixtures thereof.

2. Hydrazine containing tetramethyl thiuram monosulfide.

3. Hydrazine containing tetramethyl thiuram disulfide.

4. Hydrazine containing 2,2 dibenzothiazyl sulfide.

5. A method for repressing the dissolution of copper in hydrazine which comprises including as a solute in the hydrazine a compound selected from the group consisting of tetramethyl thiuram monosulfide, tetramethyl thiuram disulfide, 2,2 dibenzothiazyl sulfide and mixtures thereof.

6. A method for stabilizing hydrazine against decomposition including that accelerated by the presence of copper dissolved therein which involves including in the hydrazine a solute selected from the group of compounds consisting of tetramethyl thiuram monosulfide, tetramethyl thiuram disulfide, 2,2 dibenzothiazyl sulfide and mixtures thereof.

References Cited in the file of this patent

UNITED STATES PATENTS

2,502,109	Tollenaar	Mar. 28, 1950
2,680,066	Mickel et al.	June 1, 1954

OTHER REFERENCES

"The Chemistry of Hydrazine," L. F. Audrieth and B. A. Ogg, 1951 ed., pages 142, 143, John Wiley and Sons, Inc., New York.