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FOREWORD

The work described in this report was authorized under Project 1B622401A095, C/B Physical Protection Investigations (U). This work was started in February 1967 and completed in December 1967. The experimental data are recorded in notebooks MN-1978, MN-2038, MN-2039, and MN-2128.

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DIGEST

The purpose of this work was to search for a largely aqueous decontaminant for the irritants CS (o-chlorobenzylidenemalononitrile) and CS2 (CS treated with Cab-o-sil 5 and hexamethyldisilazane).

It has been found that an aqueous solution containing approximately 10% monoethanolamine (MEA) and about 0.3% of a nonionic detergent, such as Triton X-100 or Igepal CO-630, would dissolve and decontaminate CS and CS2 in soil or on cloth in about 2 minutes. Distilled or tap water may be used in the decontaminant; some tap water may require larger amounts of the detergent. The concentration of MEA could probably be decreased if a longer time for decontamination was acceptable. Once solution of the agent has taken place, decontamination is essentially complete and the decontaminant may be rinsed off with water with almost no agent or decomposition products remaining on the decontaminated surface. In typical experiments, 10 ml of decontaminant was used to detoxify 0.1 gram of CS or CS2; no attempt was made to decrease this ratio.

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I. INTRODUCTION

The chemical agent o-chlorobenzylidenemalononitrile (CS) is a slightly volatile solid, extremely irritating to eyes, nose, and lungs when dispersed as an aerosol. When this material, in powder form, is treated with a silica aerogel (Cab-o-sil 5) and hexamethyldisilazane, it is known as CS2; CS2 is more easily dispersed than is CS, and less easily wetted or caked.

The handling of CS has caused skin irritancy problems among troops required to load or disseminate the agent and has occasional informal requests for information on means of decontaminating the agent. The primary purpose of the present report is to disseminate information on the utility of an effective, inexpensive, easily produceable decontaminant for CS and CS2.

II. EXPERIMENTAL AND RESULTS

A. Materials

1. CS

2. CS2 (provided by the Dissemination Research Department, Physical Research Laboratory, Research Laboratories).

3. o-Chlorobenzaldehyde

4. Surfactants

    a. Cationic

        (1) Cetyldimethylbenzylammonium chloride

        (2) Arquad L-15 (Armour and Co.) (a quaternary ammonium compound).

        (3) Hyamine 2389 (Rohm and Haas) (methyldodecylbenzyl trimethylammonium chloride).

    b. Anionic

        (1) Sodium lauryl sulfate

        (2) Tide (Procter and Gamble) (lauryl sulfate with alkylbenzene sulfonate).

(3) Benzax 2Al (Dow Chemical Co.) (sodium dodecyldiphenyl ether disulfonate).

(4) Calgon (Calgon Corp.) (sodium hexametaphosphate).

c. Nonionic

(1) Triton X-100 (Rohm and Haas) (alkylated aryl polyether alcohol).

(2) Igepal CO-630 (Antara) (alkylated aryl polyether alcohol made by reaction of nonylphenol with nine moles of ethylene oxide).

5. Amines

a. Ethomeen L-11/25 (Armour and Co.) (a polyoxyethylated amine (primary amine converted with ethylene oxide to a tertiary amine)).

b. Monoethanolamine (referred to as MEA).

c. Diethanolamine

d. Triethanolamine

6. Laboratory reagent chemicals

7. Cloth, 8-1/2-ounce cotton sateen (olive drab, laundered, cut into 6-by 6-inch squares).

8. Soil (sandy loam)

B. Apparatus

An F&M model 400 gas chromatograph with a 1/4-inch by 6-foot glass tube and a flame ionization detector was used to analyze methylene chloride solutions of CS and its decomposition products. The chromatographic column consisted of 5% SE 30 on 60-70 mesh Chromosorb W, A?W, DMCS. Flows of helium, air, and hydrogen were each 70 ml/min. The inlet temperature was 260°, column temperature 170° and detector temperature 270°.

C. Analytical Approach

Most of the experiments reported here involved only visual olfactory detection; the latter, however, represents a closer approach to the ultimate application of the decontaminant than would chemical methods. In general, one or two people would confirm the original verdict of absence of CS odor after decontamination of cloth or soil had been accomplished.

Gas chromatography of dichloromethane extracts of treated cloth (see above) provided objective evidence of the presence of CS. Under the conditions used, the presence of as little as 0.005% of the original quantity of agent could be detected readily. Emergence times were as follows: 6 seconds for MEA and dichloromethane; 18 seconds for o-chlorobenzaldehyde; and 78 seconds for CS.

D. Orienting Experiments

Dilute aqueous solutions of a number of materials were screened for two properties; ability to wet CS2 and ability to dissolve the agent. Where solution took place rapidly, proof of agent decomposition could be sought. It was assumed, and reasonably confirmed by comparisons, that any combination of reagents capable of wetting and destroying CS2 would affect CS similarly. Table I shows the results of a series of tests using surfactants, amines and certain anions at low concentration. In each test approximately 0.2 gram of CS or CS2 was added to 20 ml of the aqueous solution of trial material. (Initial screening with CS eliminated the less effective wetting agents). Where wetting occurred, the powdery material sank quickly into the aqueous medium; otherwise it floated on top. A difference was sometimes found between tap water and distilled water, for which reason the type of water is noted. Dissolution was readily observed, since the small amount of Cab-o-sil 5 coating was insufficient to cause observable turbidity. It is to be noted that after the decontaminants containing only Ethomeen L-11/25 or only Triton X-100 had been in contact with CS2 for an hour, about half the agent had been hydrolyzed, as shown by isolation of the o-chlorobenzaldehyde phenylhydrazone derivative. (See below).

Although the 0.2% Triton X-100 combination with 0.1% NaOH looked useful, this combination might be too corrosive for many applications; moreover, the molar concentration of the base was so low that neutralization by acidic materials on the surface to be decontaminated might destroy the ability to decontaminate. For this reason, MEA was tested. By itself, MEA did not dissolve CS2 easily, but did very well when 0.2% of Triton X-100

Table I. Results of Orienting Experiments on Wetting and Solution of CS and CS2 With Aqueous Solutions

Form of agent	Type of water	Additive	Observations
CS	Distilled	Cetyldimethylbenzylammonium chloride (5%)	Wet instantly
CS2	Distilled	Cetyldimethylbenzylammonium chloride (0.25%)	Wet instantly
CS2	Tap	Cetyldimethylbenzylammonium chloride (0.25%)	Wet poorly
CS	Distilled	Arquad L-15 (5%)	Wet easily
CS	Distilled	Hyamine 2389 (2.5%)	Wet instantly
CS	Distilled	Hyamine 2389 (0.25%)	Wet slowly
CS	Distilled	Sodium lauryl sulfate (5%)	Wet easily
CS	Distilled	Tide (5%)	Wet easily
CS	Distilled	Benax 2A1 (5%)	Wet quickly
CS	Distilled	Calgon (5%)	Wet very poorly
CS2	Distilled	Na_3PO_4 (0.5%)	No wetting
CS2	Distilled	Na_2CO_3 (0.5%)	No wetting
CS	Distilled	$NaHSO_3$ (5%)	No wetting
CS2	Tap	NaOH (0.1%)	No wetting
CS2	Tap	Triton X-100 (0.2%)	Wet instantly
CS2	Tap	Triton X-100 (0.2%); NaOH (0.1%)	Wet instantly, dissolved in 5 min.
CS2	Tap	Igepal CO-630 (0.2%); NaOH (0.1%)	Wet instantly, dissolved in 5 min.
CS2	Tap	Triton X-100 (0.2%); Na_2CO_3 (0.1%)	Wet quickly, pH 11 not dissolved in 1 hr.
CS	Distilled	Ethylene glycol (5%)	No wetting
CS2	Tap	Ethomeen L-11/25 (0.25%)	Wet easily pH 9.7
CS	Distilled	MEA (5%)	Wet instantly, pH 10.8, dissolved in 5 min.
CS	Distilled	MEA (2.5%)	Wet easily
CS	Distilled	MEA (1%)	Wet poorly
CS2	Distilled	Diethanolamine (9%)	Wet in 1.5 min. no solution
CS	Distilled	Triethanolamine (5%)	Wet poorly

or Igepal CO-630 was added. The concentration of MEA was varied in order to achieve about 30 seconds wetting time when 0.1 gram of CS2 (or CS) was added to 15 ml. of decontaminant solution. Wetting times are shown in tables II through IV. Based on these data, 10% MEA was selected for use in further tests.

Table II. Addition of 0.1 Gram of CS to Mixtures of Distilled Water and MEA Containing 0.2% Triton X-100

Volume of water	Volume of MEA	pH	Time for solution
ml	ml		sec
10.0	5.0	11.6	0
11.0	4.0	11.5	0
12.0	3.0	11.3	10
13.0	2.0	11.1	120
14.0	1.0	11.0	150
14.5	0.5	10.7	420

Table III. Addition of 0.1 Gram of CS2 to Mixtures of Distilled Water and MEA Containing 0.2% Triton X-100

Volume of Water	Volume of MEA	pH	Time for solution
ml	ml	12.0	sec
10.0	5.0	12.0	15
11.0	4.0	11.7	15
12.0	3.0	11.5	17
13.0	2.0	11.4	20
14.0	1.0	11.1	45
14.5	0.5	10.9	90

Table IV. Addition of 0.1 Gram of CS2 to Mixtures of Distilled Water and MEA Containing 0.05 Gram of Igepal CO-630

Volume of water	Kind of Water	Volume of MEA	Time
ml		ml	sec
10	Distilled	0	30 for suspension
10	Tap	0	60 for suspension
10	Distilled	1	30 for solution
10	Tap	1	60 for solution

It was shown that o-chlorobenzaldehyde was one of the major products of the reaction of aqueous MEA with CS in the following way: A mixture of 0.06 gram of Triton X-100, 12 ml of MEA and 120 ml of water was added to 0.98 gram (0.0052 mole) of CS2. Solution occurred in less than 1 minute. The solution stood 10 minutes (color but no turbidity), and was then extracted with 100 ml of ethyl ether. The ether was permitted to evaporate and the residue dissolved in 20 ml of methanol. To this was added 50 ml of 0.1 N aqueous phenylhydrazine hydrochloride (0.005 mole), and the mixture permitted to stand 1 hour. A gummy, partly solid reddish precipitate had formed, from which the aqueous-alcoholic solvent was not decanted. The gummy solid was recrystallized twice from aqueous ethanol to give, with much loss, 0.33 gram of the phenylhydrazone (27.4% of theoretical yield). One more recrystallization gave m.p. 82.2°-84°. Authentic phenylhydrazone was prepared, m.p. 81.2°-83.2°, mixed m.p. 82°-84°.

In a typical experiment as performed above, the time required to dissolve the sample of CS was about 30 seconds, and a clear almost colorless solution resulted. Within 5 minutes, the solution had become distinctly yellow, then orange. After about 10 minutes, turbidity was noticeable, and by 20 minutes a precipitate had formed.

In two sets of experiments, it was attempted to follow the decomposition of CS by extraction with methylene chloride and gas chromatography of the extracts. The first set involved acidification of the decontamination mixture with hydrochloric acid to pH 1.7 prior to extraction. In the second set, the decontamination mixture was left at pH 11.5 and extracted. In both cases, CS was recovered in considerable quantity, showing a slow decrease over a period of 80 minutes to about a third of the initial amount. It is not possible to say, at this time, whether the recovery of CS is due to reformation from aldehyde and malononitrile, from a complex with MEA, or from a compound with MEA.

E. Evaluation of Decontaminants

CS or CS2 was applied (0.1 gram) to pieces of cloth and rubbed in well with a rubber glove-covered finger. The decontaminant (10 or 20 ml) was either poured on dropwise or sponged in. Most experiments involved aqueous solutions of 10% MEA and 0.3% Triton X-100 (distilled water), although in some experiments MEA ranged from 7% to 14%. After 10 minutes, the cloth was rinsed gently in at least 100 to 200 ml of tap water. The pieces of cloth were hung up in a hood to dry for 30 minutes and examined by olfaction. In no case could any residual odor of CS be detected. When, by contrast, water, with or without Triton X-100, was used in place of the decontaminant, dried cloths were still visibly contaminated and reeked of CS. In later experiments, where the period between application of decontaminant and rinsing was decreased to 2 minutes, the decontamination seemed to be just as effective as with 10 minutes contact time, but a 1 minute contact time was not quite sufficient.

An attempt was made to treat soil containing CS2 with an aqueous solution of 0.2% Triton X-100 and 0.1% sodium hydroxide. One hundred milliliters of this decontaminant was sprayed on 600 grams of soil (300 sq cm area) contaminated with 2.0 grams of CS2. After the soild had dried, the odor of CS was much in evidence.

When 33 grams of soil on a Buchner funnel (133-sq cm area) was contaminated on the surface with 0.1 gram of CS2, and 10 ml of 10% aqueous MEA (distilled water)containing 0.3% Triton X-100 poured on, the soil completely wetted. After the soil had dried out, no CS odor could be detected.

In a larger-scale experiment, a 1-sq ft. pan was filled to a depth of 2½ inches with soil (3.8 kg) and contaminated over the surface with t.4 grams of CS2. About 700 ml of decontaminant solution (10% MEA and 0.3% Triton X-100 in water) was required to wet the entire surface. Within about 2 minutes, all odor of CS was gone. The odor of o-chlorobenzaldehyde could then be detected, but was not particularly offensive. Even after standing for a day, the soil did not become entirely dry; nor could CS be smelled.

The following series of experiments provided quantitative evidence of the efficacy of decontamination of cloth contaminated with 0.1 gram of CS2. In each case, treatment of the cloth was followed by drying for 30 minutes (if necessary) and extraction with about 90 ml of methylene chloride; the solvent was evaporated down to 10 ml and analyzed by gas chromatography. The results (table II) indicated essentially complete decontamination when 20 ml of the aqueous decontaminant solution (distilled water) containing 10% MEA and 0.3% Triton X-100 was sponged on. The period between the application of decontaminant and the water rinse was 2 minutes.

Table V. Decontamination From Cloth of 0.1 gram of CS2

Treatment	CS recovered* %
None	74, 65, 77
Water in place of decontaminant	16, 29, 26
0.3% Aqueous Triton X-100 in place of decontaminant	16, 18, 19
Full decontaminant	0.008, 0.008, 0.005

*Results of triplicate experiments.

F. Observation of Skin Decontamination

During the course of this work, CS2 was evidently deposited on the face of one of the authors. The symptoms, namely burning and itching, were quite noticeable. Some MEA-containing decontaminant was applied to the affected area, left on for a few minutes and rinsed off. Immediately on application of the decontaminant, the burning and itching ceased. There was no reddening of the skin or other evidence of irritation after removal of the decontaminant.

III. DISCUSSION

This work was undertaken with a very practical short-range objective; namely, to find a good decontaminant. For this reason, most of the experiments have been devoted to demonstrating effectiveness; very little has been done to optimize the system or explore alternatives; and only a minimum of effort has been made to establish the chemical nature of the reactions involved. A 10% solution of monoethanolamine in water containing 0.2% to 0.3% of Triton X-100 has been shown an effective decontaminant for CS; moreover, in the opinion of the authors, it is far less likely to have an adverse effect on skin and material than such standard decontaminants as DS-2 solution.

Although it was ascertained that hydrolysis of CS to o-chlorobenzaldehyde occurs in the decontamination reaction, the real criterion for decontamination of CS or CS2 on cloth and soil was disappearance of the odor of the agents; this is the ultimate test of effectiveness. At the same time that the odor was lost, the white powdery deposit also disappeared; control samples of contaminated cloth or soil, not exposed to the decontaminant but rinsed with water, and other samples exposed to solutions of Triton X-100 and rinsed with water, left unmistakeable residues of the agents after drying.

The period of 10 minutes between wetting by the decontaminant of a CS-containing cloth or soil sample and the water rinse was probably far longer than necessary, and might be reduced to 2 minutes. It is also possible that the water rinse might be omitted for many applications.

Even untreated CS, and certainly CS2, is not readily wetted by water alone, and, if in solution, is not very rapidly hydrolyzed; thus, more than water is required to effect decontamination. It is quite probable that the function of Triton X-100 is mainly as a detergent that helps dissolve the agent; no chemical attack on the CS molecule can take place unless it is in solution.

Monoethanolamine must certainly act as a nucleophilic reagent, in which role it is by no means unique. Thus, for example, cyanide ion,[1,2] thiolate ions,[2,3] and hypochlorite ion[4] attack the activated ethylenic pi bond of CS. There is evidence[3] that a dialkylamino function in the same molecule catalyzes the addition of a mercaptan to the ethylenic bond of CS, or perhaps adds to that bond first, and then rearranges to give the sulfide bond. In the case of the addition of monoethanolamine to acrylonitrile,[5] it is certainly the amine function which adds. In the examples cited above, as well as in the addition of tributylphosphine,[6] reaction stops with addition of the nucleophile to the double bond. In other instances, notably ordinary hydrolysis (which probably involves hydroxide ion attack in the first step), the sigma bond of the original ethylenic bond of CS is finally cleaved,[7,8] resulting in the formation of o-chlorobenzaldehyde and the malononitrile anion. Apparently, hydrolytic cleavage can also be catalyzed by glycine[8]. In the present instance, in which aldehyde (as the phenylhydrazone) was recovered, the reaction can also be considered a catalyzed hydrolysis.

The rapid solution of CS in 10% aqueous monoethanolamine can hardly be explained on the basis of simple increased solvency because of the presence of an organic solvent, as compared to the solvency of pure water. The water solubility of CS is low, probably not much greater than 0.02%,[9] whereas, the present experiments involved formation of 1% solutions in 30 seconds without stirring. Following solution, the mixtures become cloudy after lapses of 10 to 20 minutes. These observations can best be explained by initial nucleophilic addition of monoethanolamine to the olefinic bond, followed by further reaction ending in carbon-carbon cleavage. The addition compound must be water-soluble although the final products are not. These explanations are in consonance with the literature cited above.

IV. CONCLUSIONS

It has been found that an aqueous solution containing approximately 10% monoethanolamine (MEA) and about 0.3% of a nonionic detergent, such as Triton X-100 or Igepal CO-630, would dissolve and decontaminate CS and CS2 in soil or on cloth in about 2 minutes. Distilled or tap water may be used in the decontaminant; some tap water may require larger amounts of the detergent. The concentration of MEA could probably be decreased if a longer time for decontamination was acceptable. Once solution of the agent has taken place, decontamination is essentially complete and the decontaminant may be rinsed off with water, with almost no agent or decomposition products remaining on the decontaminated surface. In typical experiments, 10 ml of decontaminant was used to detoxify 0.1 gram of CS or CS2; no attempt was made to decrease this ratio.

LITERATURE CITED

1. Corson, B.B., and Stoughton, R.W. Reactions of Alpha, Beta-Unsaturated Dinitriles. J. Am. Chem. Soc. 50, 2825 (1928).

2. Sass, S., Davis, P.M., Master, I., Reynolds, R.A., Roberts, E., Sechrist, J., and Beitsch, N. CWLR 2396. Analytical Methods for CS. Part II. Volumetric Determination of CS Purity; Estimation of Total Volatiles in CS. May 1960. UNCLASSIFIED Report

3. Tarantino, P.A., and Sass, S. EATR 4104. An Investigation of the Rates of Reaction of Benzalmalononitriles and Other Irritants With 2-Diethylaminoethyl Mercaptan (DEAM), Employing Controlled-Potential DC Polarography. I. Polarography and Rates of Reaction of DEAM With CS. July 1967. UNCLASSIFIED Report.

4. Rosenblatt, D.H., and Broome, G.H. Directo Epoxidation of o-Chlorobenzylidenemalononitrile With Hypochlorite Ion. J. Org. Chem. 28, 1290 (1963).

5. Adams, R., Ed. Organic Reactions. Vol. V. p.85. John Wiley and Sons, Inc., New York, New York 1949.

6. Rappoport, Z., and Gertler, S. Nucleophilic Attacks on Carbon-Carbon Double Bonds. Part IX. The Primary (Equilibrium) Step. The Reaction of Tri-n-butylphosphine With Arylmethylenemalononitriles in Methanol, J. Chem. Soc. 1360 (1964).

7. Patai, S., and Rappoport, Z., Nucleophilic Attacks on Carbon-Carbon Double Bonds. Part II. Cleavage of Arylmethylenemalononitriles by Water in 95% Ethanol. J. Chem. Soc., 383 (1962)

8. Hutton, E., and Tees, T.F.S., Porton Technical Paper 806. The Rates of Hydrolysis of Some Substituted Benzalmalononitriles. April 1962. RESTRICTED Report

9. Sass, S., Master, I., Martin, J.J. and Matoushek, R., CWLR 2393. Methods forAnalysis of CS. Part I. Colorimetric Methods for Trace Analysis of CS and Its Impurities; Hydrolysis of Dilute Solutions of CS. March 1960. UNCLASSIFIED Report.