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SULFAMIC ACID CLEANING SOLUTION
FOR 4,4' METHYLENE-BIS-ORTHO-
CHLOROANILINE (MOCA)

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OAK RIDGE Y-12 PLANT
OAK RIDGE, TENNESSEE

prepared for the U.S. ATOMIC ENERGY COMMISSION
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**SULFAMIC ACID CLEANING SOLUTION FOR
4,4' METHYLENE-BIS-ORTHO-CHLOROANILINE (MOCA)**

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ABSTRACT

An aqueous solution of sulfamic acid was developed for decontaminating MOCA-contaminated surfaces to less than the analytical detectable limits for MOCA. No flammability hazards were experienced.

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SUMMARY

Laboratory tests have shown that an aqueous solution of 1.0 wt % sulfamic acid-0.5 vol % surfactant can be used for decontaminating MOCA-contaminated surfaces to less than the analytical detectable limits for MOCA, without any flammability hazards.

Nuclear magnetic resonance spectra have shown that a different compound is formed when sulfamic acid is reacted with MOCA, as evidenced by the disappearance of the NH_2 peak from the MOCA spectrum.

INTRODUCTION

Methylene-bis-ortho-chloroaniline, MOCA, is used as a curing agent in the manufacture of urethane-elastomer materials such as Adiprene L-100 and epoxy resins. Recently, MOCA was declared to be a cancer-causing agent by the Occupational Safety and Health Administration (OSHA),⁽¹⁾ and its use at various industrial plants in the United States has been restricted or curtailed.

MOCA, as used at the Oak Ridge Y-12 Plant,^(a) consists of a fine powder that is relatively insoluble in water. A summary of the physical and chemical properties of MOCA is given in Table 1. Although MOCA is highly soluble in such organic solvents as acetone, methyl ethyl ketone, toluene, and others, these solvents present flammability and/or toxicity hazards and are thus unsatisfactory for use in plant areas where electrical machinery and other spark or ignition sources are present. Laboratory studies were made to find a suitable nonflammable, easy-to-use decontaminating solution for MOCA that would permit a cleanup of MOCA-contaminated surfaces (eg, walls, worktable tops, and gloves) around the plant manufacturing and usage areas so that a wipe test and analytical determination by gas chromatography would no longer show any MOCA to be present.

Table 1
PHYSICAL AND CHEMICAL PROPERTIES OF MOCA

Chemical Composition	4,4'-methylene-bis (2-chloroaniline)	
Structural Formula
Physical Form	fine powder (100% through 40 mesh screen)	
Color	light tan	
Specific Gravity	1.39	
Odor	none	
Storage Stability	excellent; slightly hygroscopic	
Melting Range	212 - 221° F (100 - 105° C)	
Moisture Content	< 0.5%	
Solubility	<u>Solvent</u>	<u>Weight Percent</u>
	Toluene	7.5
	Methylene Ethyl Ketone	51.0
	Mesityl Oxide	43.0
	Cellosolve Acetate	34.4
	Tetrahydrofuran	55.5
	Trichloroethylene	4.2
	Dimethylformamide	61.7

(a) Operated by the Union Carbide Corporation's Nuclear Division for the US Atomic Energy Commission.

CLEANING SOLUTION FOR MOCA

EXPERIMENTAL WORK AND RESULTS

Preliminary solubility studies were made with MOCA, using six candidate aqueous solutions to determine their relative abilities for solubilizing MOCA. These studies were made by adding 500-milligram quantities of MOCA to 100-milliliter volumes of various aqueous solutions in glass-stoppered Erlenmeyer flasks. After contact for 48 hours at room temperature, it was observed that the initial 500 milligrams of MOCA powder that was in contact with a 5 wt % sulfamic acid solution had dissolved completely, whereas some undissolved MOCA was still visible in the other four candidate decontaminating solutions. Thus, of the candidate aqueous solutions listed in Table 2, a 5 wt % sulfamic acid was shown to give the highest MOCA solubility (ie, > 0.5%).

Table 2
AQUEOUS DECONTAMINATING SOLUTIONS EVALUATED
FOR MOCA SOLUBILITY

1. Ethylenediamine Tetra Acetic Acid ⁽¹⁾	-	2 Wt %
2. Acetic Acid	-	5 Wt %
3. Ethylenediamine Tetramethyl Phosphonic Acid	-	2 Wt %
4. Tartaric Acid	-	2 Wt %
5. Sodium Hypochlorite	-	8.5% Cl ₂ Content
6. Sulfamic Acid	-	5 Wt %

(1) Demineralized water was used for all solutions.

MOCA decontamination studies were made on stainless steel surfaces using aqueous sulfamic acid and other candidate solutions. Results, as summarized in Table 3, showed that a 1.0 wt % sulfamic acid-0.5 vol % liquid surfactant solution was the most effective. MOCA-contaminated surfaces were cleaned to less than the detectable limit of 10 μ g MOCA, as determined by standard wipe tests and gas chromatography analyses.

For the MOCA decontamination studies summarized in Table 3, a "standard" solution of MOCA was prepared by dissolving a weighed amount of MOCA in 100 milliliters of acetone. Aliquots from this MOCA solution were then applied to a 5 by 5-inch surface of stainless steel using a graduated pipette so that a total of 175 μ g of MOCA was distributed uniformly over the surface of the stainless steel. After evaporation of the acetone, the surface was cleaned by either wiping it lightly using a cellulose sponge containing the candidate decontaminating solution, or by applying the candidate decontaminating solution onto the metal surface held at a 45° angle by squeezing from a polyethylene bottle. The entire stainless steel surface was then wiped with a one-inch-diameter cellulose filter paper disc dampened with isopropyl alcohol. The MOCA content of the disc was analyzed by gas chromatography. The limit of detection of this method for MOCA is 10 μ g.

Nuclear magnetic resonance spectra obtained on MOCA and the sulfamic acid derivative of MOCA are compared in Figures 1 and 2, respectively. The most upfield peak found in the

Table 3
SUMMARY OF MOCA DECONTAMINATION TESTS

Decontaminating Solution	Surface Contamination after Application ($\mu\text{g MOCA}$)	Decontamination Factor ⁽¹⁾ (%)
<u>Cellulose Sponge Application of Solution</u>		
None	175	0.0
Sodium Hypochlorite (8 wt %)	110	37.1
Zinc Chloride (4 wt %)	105	40.0
Anionic Surfactant ⁽²⁾ (2 vol %)	30	83.0
Sulfamic Acid (5 wt %)	< 10	94.3 ⁽³⁾
<u>Polyethylene Wash Bottle Application of Solution</u>		
Sulfamic Acid (2 wt %) - Anionic Surfactant ⁽²⁾ (0.5 vol %)	< 10	94.3 ⁽³⁾
Sulfamic Acid (2 wt %) - Nonionic Surfactant ⁽⁴⁾ (0.5 vol %)	< 10	94.3 ⁽³⁾
Sulfamic Acid (1 wt %) - Anionic Surfactant ⁽²⁾ (0.5 vol %)	< 10	94.3 ⁽³⁾
Sulfamic Acid (1 wt %) - Nonionic Surfactant ⁽⁴⁾ (0.5 vol %)	< 10	94.3 ⁽³⁾

(1) Decontamination Factor (%) =

$$\frac{\mu\text{g MOCA on Surface Before Cleaning} - \mu\text{g MOCA on Surface After Cleaning}}{\mu\text{g MOCA on Surface Before Cleaning}} \times 100.$$

(2) A mixture of ammonium ethoxylated alcohol sulfate, sodium alkylbenzene sulfonate, sodium xylene sulfonate, sodium sulfate, and sodium hydroxyethylene diamine triacetate in demineralized water.

(3) Based on the maximum possible value of 10 μg s MOCA left on the surface.

(4) A product of the Onyx Chemical Company.

MOCA and sulfamic acid-treated MOCA spectra was located at 2.5 ppm^(b) and corresponds to dimethylsulfoxide used as a solvent in the NMR studies. The NH_2 peak of MOCA was found at 3.36 ppm; the CH_2 peak was found at 3.59 ppm. The peak for water was located at 5.09 ppm, and the aromatic hydrogen peaks were located at 6.5 to 7.3 ppm.

As shown in Figure 2, when one equivalent of sulfamic acid was added to MOCA it tied up the NH_2 and formed a salt, as evidenced by the lack of NH_2 in the sulfamic acid-treated MOCA spectrum. The water peak also broadened considerably. Protons of the MOCA-sulfamic acid salt were barely detectable in the baseline since the peak was so broad (3 to 6.5 ppm).

Upon treating MOCA with one equivalent of sulfamic acid and adding sodium hydroxide to attain an alkaline pH, it was found by nuclear magnetic resonance spectrometry that the MOCA-sulfamic acid adduct did not revert back to the original MOCA spectrum and that the water peak had broadened very considerably. This nonreversion of the sulfamic acid-treated MOCA back to MOCA even at an alkaline pH may be significant in that it

(b) Unit of chemical shift difference in the shielding constant.

Figure 1. NUCLEAR MAGNETIC RESONANCE SPECTRUM OF MOCA

Figure 2. NUCLEAR MAGNETIC RESONANCE SPECTRUM OF MOCA AFTER THE ADDITION OF SULFAMIC ACID.

indicates that the carcinogenic and/or toxicological properties of the MOCA may also have been altered. Further research would be required to substantiate this assumption.

It has been reported⁽²⁾ that primary, secondary, and tertiary amines react with sulfamic acid by addition to form amine sulfamates; eg:

DISCUSSION

Solubility and decontamination studies with MOCA were carried out under controlled procedures which conformed to OSHA regulations on the handling of carcinogenic materials.

By definition,⁽³⁾ decontamination is "the safe removal from the work environment or inactivation of a carcinogen to eliminate residual carcinogen as detectable by the most sensitive, feasible sampling and analytical methods available". The aqueous 1.0 wt % sulfamic acid-0.5 vol % surfactant decontaminating solution listed in Table 3 offers industries using MOCA in manufacturing processes and development programs a nonflammable cleaning solution for removing the compound from equipment and working areas.

In conjunction with the use of aqueous sulfamic acid solutions for MOCA decontamination, a rapid color test is used in Y-12⁽⁴⁾ for the detection of MOCA by itself and in MOCA-cured Adiprene L-100 resin. MOCA, when impregnated on polyester spunbonded paper or polyester cloth, reacted with chloranil in chlorobenzene to yield a blue color with an intensity proportional to the MOCA content. The lower limit of detection of this test was about 25 μg MOCA. This method could be used in conjunction with sulfamic acid decontamination of MOCA in plant areas.

As reported in Table 3, the concentration of sulfamic acid was reduced from 5.0 to 1.0 wt %, with no measurable loss in the ability of the solution to decontaminate MOCA to less than the detectable limit of the analytical method. Since sulfamic acid is the active chemical decontaminating agent, Table 3 also shows that there was no detectable difference in the effectiveness of the decontaminating solutions by changing the type of surfactant or wetting agent that was used; ie, whether the surfactant was of the anionic or nonionic type.

Recent DuPont studies⁽⁵⁾ on the physiological hazards and exposure control of MOCA have shown that biological monitoring by urinalysis in conjunction with gas chromatography provided a reliable and expedient control system for monitoring personnel exposures to MOCA. On the basis of its extremely low solubility in water, removal of MOCA as a body burden by urinary excretion would be expected to be a slow process. It is suggested that the urinary excretion level may be increased appreciably by ingestion of small quantities of sulfamic acid to increase the solubility of MOCA in the aqueous human biological system.

Medical aspects of sulfamic acid ingestion for this purpose would, of course, require additional studies which are beyond the scope of the current investigation.

In a study on the toxicology of sulfamic acid and its derivatives made by the Haskell Laboratory of Industrial Toxicology it was concluded that the continued oral ingestion of sulfamic acid or ammonium sulfamate by female white rats for 105 days produced no deleterious effect on animals receiving up to 1% of either compound in the diet.⁽²⁾

CONCLUSIONS

As a result of this study, the following conclusions were reached:

1. An aqueous solution of sulfamic acid containing a surfactant has been shown to be an effective and nonflammable solubilizing and cleaning agent for MOCA in plant operating areas where electrical machinery and other spark or ignition hazards may be present.
2. Aqueous solutions of sulfamic acid containing a surfactant can decontaminate MOCA to less than the best method of analytical detection; ie, less than 10 μg MOCA per 25 square inches of contaminated surface area.
3. Nuclear magnetic resonance (NMR) studies have shown that when sulfamic acid is reacted with MOCA, a salt compound is formed that changes the NMR spectrum of the MOCA as evidenced by a disappearance of the NH_2 peak at 3.36 ppm in the MOCA spectrum. This change in the MOCA spectrum thus indicates that the chemical properties and possibly the carcinogenic and toxicological properties of MOCA may also be altered by sulfamic acid treatment.

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