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NCBC GULFPORT
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LETTER FROM U S AIR FORCE REGARDING BACKGROUND CHEMICAL TECHNOLOGY FOR ON SITE TREATMENT NCBC GULFPORT MS
1/4/1985
U S AIR FORCE HEADQUARTERS

DEPARTMENT OF THE AIR FORCE
HEADQUARTERS AIR FORCE ENGINEERING AND SERVICES CENTER
TYNDALL AIR FORCE BASE, FL 32403

JAN 04 1985

REPLY TO
ATTN OF: RD

SUBJECT: Herbicide Orange Site Demonstrations

TO: Commander
Naval Construction Battalion Center
Gulfport, Mississippi 39501

1. Capt Stoddart has informed me of the concerns you expressed on 21 Dec 84 during the site demonstration briefing. To respond to your concerns Capt Stoddart has prepared a briefing on the chemical restoration technology (AMPA) for presentation to you on 10 Jan 85.

2. To support the AFESC's recommendation on the chemical technology, I am enclosing copies of two background papers. These documents should provide you with additional technical information prior to the scheduled briefing. In addition, a comprehensive package of technical support data will be hand carried to your technical staff.

3. The Engineering and Services Laboratory is convinced that the chemical technology offers a potential cost-effective alternative for restoring Herbicide Orange contaminated sites. The research plan for chemical technology demonstration provides for preliminary laboratory studies to identify reaction by-products. The results of this study will serve as a decision point prior to initiating actual site demonstration.

4. Your concurrence on the proposed chemical technology demonstration will greatly enhance the current Herbicide Orange R&D program. I look forward to working with you in resolving the complex environmental problems associated with Herbicide Orange/dioxin contaminated sites.

Robert E. Boyer

ROBERT E. BOYER, Colonel, USAF
Director, Engineering & Services Laboratory

2 Atch
1. AMPA Background Paper
2. A-PEG Background Paper

BACKGROUND PAPER
ON
SITE DEMONSTRATION
In Place Treatment by Chemical Methods

AMPA

Technology Summary

This in situ treatment process involves the direct contact of the Alkaline Metal Polyglycoxide and additives to 2,3,7,8 TCDD. The strongly nucleophilic reagent displaces chlorine atoms on the dioxin ring; increasing solubility and decreasing toxicity.

Scientific Support

The ability of sodium and potassium polyalkoxides and radical additives to displace chlorine atoms from aromatic halides such as polychlorinated biphenyls has been demonstrated. The similar reaction has been verified on TCDD and on TCDD-contaminated materials from the Icmesa plant of Seveso, Italy. These reactions proceed near ambient conditions, in the presence of reasonable concentrations of water, and, most importantly, yield reaction products that are nontoxic.

The reagent consists of three major components:

- A polyglycol copolymer of ehtylene oxide (EO) and propylene oxide (PO) in the range of molecular weight, i.e., a sodium salt of a reagent of molecular weight 6000 gives a nucleophilic displacement rate about 10 times faster than tetraethylene glycol. The viscosity of the reagent varies with molecular weight so that the reagent can be adapted to tasks that require varying degrees of penetration into solid surfaces. For example, one of those reagents penetrates concrete and appears to be suited particularly well for testing on the coral rocks at JI.

- A base that may be MOH (sodium or potassium hydroxide) or M_2CO_3, the corresponding carbonate.

- A radical source such as sodium peroxide at 1-5 percent w/w, or ultraviolet radiation. In the case of reactions with solids, penetrating agents such as those used in pesticide formulations are added.

Destruction of Polychlorinated Biphenyls (PCBs) -- Sixteen ml of mineral oil containing 20,000 ppm PCB was placed into a 50-ml flask. To the solution, maintained at 85°, was added 2.0 g of carbowax-6000, 0.5 g of potassium carbonate, and 0.2 g of sodium peroxide. The mixture was stirred magnetically for 3 hours, cooled, and analyzed by capillary GC/EC. The residual PCB concentration was 95 ppm, a reduction of 99.5 percent.

In similar experiments, 0.1 ml (4 percent) and 0.3 ml (11 percent) of water was added. The addition of 4 percent of water to the reagent had little effect on the reaction rate, yielding a residual PCB concentration of 140 ppm, a 99.3 percent reduction. The addition of 11 percent water to the reagent decreased the reaction rate to yield a residual PCB concentration of 1380 ppm. However, 93.1 percent reduction was effected.

Destruction of TCDD in Solvent -- A solution of 4.0 ml of n-decane containing 4 ppb of 2,3,7,8-TCDD was stirred for 2 hours at 85° in the presence of 1.0 g of carbowax-6000, 0.5 g of potassium carbonate, and 0.1 g of sodium peroxide. Analysis by GC-MS detected no residual TCDD, a destruction of 98 percent. These data confirm that TCDD decomposition occurs readily at 50° in solution but that room temperature reactions are slower as expected.

Destruction of TCDD in Solids -- Destruction of TCDD in solids by the AMPA reagent has been tested on contaminated metal pipe and soil from Seveso. A piece of pipe, 4 inches in diameter and 4 inches long, from the discharge of the Icmesa plant vent condenser, showed brown incrustration on the inner surface and contained 3.73 ppm TCDD plus trichlorophenol and other reaction products from the exothermic reaction. The pipe was immersed in a vessel containing 400 g of AMPA reagent. The mixture was stirred by ultrasound for 5 hours at 55°. At the end of this period, the pipe's visible incrustration had disappeared, and the total residual TCDD concentration was 0.09 ppm, a destruction of 97.5 percent.

Soil from Seveso Zone A, 263 g, containing 513 ppt of TCDD, was stirred with 977 g of AMPA reagent for 6 hours at 85°. The soil's dioxin concentration was 97 ppt, 81 percent destruction.

Reaction Products -- Knoweldge of reaction products and their toxicological environmental impact is crucial to any dioxin destruction process.

To a mixture of 12.5 g of AMPA reagent at 80° was added 2 mg of TCDD. Samples were taken at 5 minutes, and 1,2,3, and 5 hours for chemical analysis, and at 60, 105, and 300 minutes for toxicological analysis.

Chemical analysis after 5 minutes of reaction showed products of progressive dechlorination, moni-, di-, and trichlorodibenzodioxins plus TCDD. After one hour, trace amounts of chlorinated dioxins were observed in addition to nonchlorine containing peaks at m/e = 647 and 662, presumably glycol condensation products. Thus, the reaction appears to proceed by two pahtways, reductive dechlorination presumably via radical intermediates and nucleophilic substitution presumably via alkoxides.

Toxicological testing was carried out by H. Poiger at the Federal Institute of Technology, Switzerland, using male guinea pigs. Animals were dosed by gavage, weighed at appropriate intervals, and checked for toxic signs before and after sacrificing. The conclusions from this experiment are:

"Neither the typical signs of intoxication with chlorinated dioxins, like retardation of growth or decreased thymus weight, nor other toxic signs were observed within the experimental period. This was at does levels of 431 and 661 cmg of "TCDD-equivalents"/kg body weight. The acute toxicity LD_{50} TCDD in the guinea pig is at approximately 1 cmg bw (0.6 and 2 cmg bw have been reported). In view of this absence of any sign of acute toxicity at 431 and 661 fold dose level (of the degradation products) it can be assumed that the LC_{50} of these products is higher than 660 cmg/kg bw."

These results demonstrate significant decrease in toxicity of TCDD upon treatment with AMPA reagent.

<u>Quantity of Soil to be Tested</u>

- 10 x 20 foot plot

  -- Time on site, approximately 30-45 days.

HQ AFESC/RDVW
Capt Stoddart/AUTOVON 970-2942
12 Dec 84

BACKGROUND PAPER
ON
SITE DEMONSTRATION IN-PLACE TREATMENT BY CHEMICAL METHODS
A-PEG

1. REAGENTS: KOH/PEG

KOH - Potassium Hydroxide

- Strong base

- Easily neutralized with acid

PEG - Polyethyleneglycol

- $HOCH_2\ (CH_2OCH_2)_n\ CH_2OH$

- Commonly used in a variety of industries as emulsifiers, dispersants, detergents, plasticizers and lubricants.

- In particular, used in cosmetics/toiletries such as creams, lotions, deodorants + lipstick.

- Also used in pharmaceutical industry, in capsules and tablet coatings.

- Extensive research at EPA/Cincinnati has concluded that PEG's are nontoxic.

- Union Carbide PEG Material Safety Data Sheets are attached.

2. REACTION ENDPRODUCTS.

- KOH/EPG detoxifies dioxin by replacing one or more chlorine atoms with glycol chains.

- KCl - Potassium Chloride

- nontoxic salt

- Dioxin-PEG complex

- no toxicology studies to date done on this compound

- Toxicology studies have been done on a similar compound, the reaction product of Polychlorinated biphenyls and KOH/PEG.

o Study by GE of toxicology of PEG and PCB-PEG compounds. (Brunelle + Singleton, 1983)

o Oral ingestion (max-dose 5,000 mg/kg, rat)

o Dermal absorbtion, mice--nontoxic

o Both are mild eye irritants to rabbits

o Study at EPA/Duluth

- Arochlor 1260 - bioaccumulation occurred in fathead minnows.

- No bioaccumulation of PEG's or PCB-PEG reaction products in fathead minnows.

- EPA/Duluth gearing up for similar study using KOH/PEG - dioxin reaction products. This study will begin in March 1985. Study will be complete before any in situ study would take place at NCBC.

- EPA/Cincinnati with contractor Frankling Research Institute have applied APEG reagent to dioxin contaminated soil in a horse arena in Missouri (Nov 84).

HQ AFESC/RDVW
Lt Heyse, AUTOVON 970-4628
4 Jan 85

MATERIAL SAFETY DATA SHEET

EFFECTIVE DATE: August 31, 1981

I. IDENTIFICATION

PRODUCT NAME:	CARBOWAX® METHOXY POLYETHYLENE GLYCOL 350		
CHEMICAL NAME:	--	CHEMICAL FAMILY:	Polyethylene Glycols
FORMULA:	$CH_3O(CH_2\text{-}CH_2\text{-}O)_nH$	MOLECULAR WEIGHT:	335-365
SYNONYMS:	--		
DEPARTMENT OF TRANSPORTATION	HAZARD CLASSIFICATION	None	
	SHIPPING NAME	None	
CAS # 9004-74-4	CAS NAME	Poly(oxy-1,2-ethanediyl), α-methyl-ω-hydroxy-	

II. PHYSICAL DATA

BOILING POINT, 760 mm Hg 101.325 kPa	Decomposes	FREEZING POINT	(23 to 50 °F) −5 to 10 °C
SPECIFIC GRAVITY (H_2O = 1)	1.097 at 20/20 °C	VAPOR PRESSURE at 20 °C	< 0.007 kPa < 0.05 mm Hg
VAPOR DENSITY (air = 1)	> 1	SOLUBILITY IN WATER, % by wt.	Complete
PER CENT VOLATILES BY VOLUME	Nil	EVAPORATION RATE (Butyl Acetate = 1)	Nil
APPEARANCE AND ODOR	Clear liquid; mild characteristic odor.		

III. INGREDIENTS

MATERIAL	%	TLV (Units)	HAZARD
CARBOWAX Methoxy Polyethylene Glycol 350	100	None established	None currently established

IV. FIRE AND EXPLOSION HAZARD DATA

FLASH POINT [test method(s)]	440 °F, Cleveland open cup ASTM D 92				
FLAMMABLE LIMITS IN AIR, % by volume		LOWER	Not determined (nonvolatile fluid)	UPPER	Not determined (nonvolatile fluid)

EXTINGUISHING MEDIA	Use water spray, carbon dioxide, dry chemical, alcohol-type or universal-type foams applied by manufacturers' recommended technique.
SPECIAL FIRE FIGHTING PROCEDURES	Don't spray pool fires directly; a solid stream of water directed into hot burning liquid could cause frothing. Use supplied breathing air and protective clothing.
UNUSUAL FIRE AND EXPLOSION HAZARDS	None

EMERGENCY PHONE NUMBER

304/744-3487

This number is available days, nights, weekends, and holidays.

While Union Carbide Corporation believes that the data contained herein are factual and the opinions expressed are those of qualified experts regarding the results of the tests conducted, the data are not to be taken as a warranty or representation for which Union Carbide Corporation assumes legal responsibility. They are offered solely for your consideration, investigation, and verification. Any use of these data and information must be determined by the user to be in accordance with applicable Federal, State, and local laws and regulations.

UNION CARBIDE CORPORATION • ETHYLENE OXIDE DERIVATIVES DIVISION
OLD RIDGEBURY ROAD, DANBURY, CT 06817

V. HEALTH HAZARD DATA

T.V AND SOURCE: None established by ACGIH or OSHA.

ACUTE EFFECTS OF OVEREXPOSURE	
SWALLOWING	None currently known. May cause some nausea.
SKIN ABSORPTION	None currently known.
INHALATION	None currently known.
SKIN CONTACT	None currently known.
EYE CONTACT	None currently known.
CHRONIC EFFECTS OF OVEREXPOSURE	None currently known.
OTHER HEALTH HAZARDS	None currently known.

EMERGENCY AND FIRST AID PROCEDURES:	
SWALLOWING	No harmful effects expected.
SKIN	Wash with soap and water.
INHALATION	No emergency care anticipated.
EYES	Flush with water.

NOTES TO PHYSICIAN

Toxicology studies have shown the material to be of very low toxicity and nonirritant. There is no specific antidote. Treatment of overexposure should be directed at the control of symptoms and the clinical condition.

VI. REACTIVITY DATA

STABILITY			
UNSTABLE	STABLE	CONDITIONS TO AVOID	None
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INCOMPATIBILITY (materials to avoid)	None
HAZARDOUS COMBUSTION OR DECOMPOSITION PRODUCTS	Burning can produce carbon monoxide and/or carbon dioxide.

HAZARDOUS POLYMERIZATION			
May Occur	Will not Occur	CONDITIONS TO AVOID	None
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VII. SPILL OR LEAK PROCEDURES

STEPS TO BE TAKEN IF MATERIAL IS RELEASED OR SPILLED	Small spills should be flushed with large quantities of water. Larger spills should be collected for disposal.
WASTE DISPOSAL METHOD	Mix with flammable solvent and incinerate in a furnace where permitted under appropriate Federal, State, and local regulations.

VIII. SPECIAL PROTECTION INFORMATION

RESPIRATORY PROTECTION (specify type)	None required.
VENTILATION	General room ventilation is expected to be satisfactory.

PROTECTIVE GLOVES	Plastic	EYE PROTECTION	Safety glasses
OTHER PROTECTIVE EQUIPMENT	Eye bath and safety shower		

IX. SPECIAL PRECAUTIONS

PRECAUTIONS TO BE TAKEN IN HANDLING AND STORING

Normal precautions common to good manufacturing practice should be followed in handling and storage.

FOR INDUSTRY USE ONLY

OTHER PRECAUTIONS

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