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FORM 1076A

54540
11-26-74
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November 26, 1974

To: G. C. Woehr

From: S. M. Hall

Monthly Report For November, 1974

Vinyl Chloride

Abstract:

Removal of vinyl chloride from stack gases via chemical reaction may be a feasible method of meeting the proposed Federal permissible exposure level of 1 ppm. A search of the Chemical Abstracts has uncovered eighty possible reactants of which four or five might be applicable.

Benzene, chlorine, hydrogen chloride (with oxygen) and alkyl chlorocyclohexanes seem to react with vinyl chloride in reasonable times and at reasonable conditions (temperature, pressure) with high conversions (>90%). Study of the literature is not complete so no conclusions or recommendations are included.

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KEYWORDS: VINYL CHLORIDE POLLUTION REACTIONS

I. Discussion

The new Federal standards for vinyl chloride exposure call for a time averaged maximum of 1 ppm compared with the old standard of 500 ppm and the interim standard of 50 ppm. The new standards take effect January 1, 1975, however, it is understood that some manufacturers (particulary PVC producers) might take up to several years to meet the standards. Guidelines for air monitoring, medical examinations and respiratory equipment are applicable until the 0.5 ppm "action level" vinyl chloride standard is met. (See Federal Register 39:194 p. 53 (1974)).

One possible method of removing vinyl chloride from stack gases is to chemically react the monomer to form a harmless or easily removable chemical.

The Chemical Abstracts (Volumes 1 to date) have been searched for references to previous reaction studies. Eighty chemicals were found for which reactions with vinyl chloride have been documented (see Table 1). The vast majority of these are not applicable to the vinyl chloride pollution problem for reasons of pressure, temperature, conversion or product composition. Many of the reactions were run batchwise at high pressure for several days with the resulting vinyl chloride conversion very low (< 50%).

The reactants that seem to offer the most promise are benzene, chlorine, hydrogen chloride and alkyl chlorocyclohexanes. Original articles and patents are on order which have not yet arrived so the evaluation of these reactions is at best incomplete. Even with all literature references in hand it will probably be most difficult to obtain more than an idea of possible vinyl chloride reaction schemes without laboratory work.

1. Benzene

Two reactions are reported. The first, benzene + vinyl chloride + aluminum chloride yields 1,1-diphenylethane; 9,10-dimethyldihydroanthracene; and a tar or resin. The reaction occurs at room temperature; yields and conversions are not given. Heating the reaction is said to increase tar formation.

The other benzene reaction looks promising. Benzene + vinyl chloride + 94% H_2SO_4 (in a mole ratio of 4:1:2) react at 30°-60°C. After two hours there remains 0% halo olefin and 0% initial starting material. This is from a Russian reference, not yet received.

2. Chlorine

At least a dozen references deal with the chlorination of vinyl chloride to form dichloro- and trichloroethane. Catalytic, photochlorination batch and continuous experiments are described with yields and conversions as high as 99%.

A basic problem of chlorination is that relatively toxic (10 to 350 ppm TLV) dichloro- and trichloroethane are produced and it is likely that liquefaction or scrubbing of these materials would be necessary to achieve satisfactory pollution control.

Typical reactions:

a. "Into a jacketed tube half-stuffed with Fe shavings just covered with CH_3CCl_3 was passed dry Cl mixed with CH_2=CHCl (1:1.1 mols) at 620 cc/min. while cooling the tube to 20-25° to give almost pure CH_3CCl_3 (yield 99.2% of Cl)." Japan 158669

b. "Cl and vinyl chloride in a ratio of 1.02:1 (by volume) are passed into $ClCH_2CHCl_2$ (II) contg. .5% $FeCl_3$. The II is fed continuously into a reactor contg NaOH 1220 and H_2O 11000 parts at 65-80°, the CH_2=CCl_2 distg. off. The reaction efficiency is 90%" Brit 577876

c. "Cl_2CHCH_2Cl (I) is prepd. by adding 1 mole Cl to a little more than 1 mole CH_2=CHCl (II) in at least 20 moles I in a packed tower, with the I flowing down and the mixt of Cl and II bubbled in near the middle or bottom at 20-50° in the dark. The yields are nearly theoretical." Brit 627263.

3. Hydrogen Chloride

Several references discuss HCl addition to vinyl chloride. The product is dichloroethane; conversion is low and reaction time is long. Oxychlorination (O_2 + HCl + V.C.) achieves much better conversion, however, (as high as 93%). One patent (Neth appl. 6414743) describes a catalytic reaction in the gas phase of HCl, vinyl chloride and air (molar ratio 45:15:40) with a yield of 70.7% of 1,1,2-trichloroethane. What this means as far as conversion of vinyl chloride is concerned is uncertain.

4. Alkyl Chlorocyclohexanes

"Isomeric (B,B-dichloroethyl) methylcyclohexanes, b.80-4°, were obtained in 95% yields from the condensation of CH_2=CHCl with a mixt. of isomeric chloromethylcyclohexanes (I) in the presence of purified anhydrous $AlCl_3$ when the reaction was carried out at -15° to -20° for 30-5 min. with 4-5% $AlCl_3$ based on I and a I-CH_2=CHCl molar ratio of 3:1." C.A. 64:15758c

II. Future Work

The literature will be studied to determine what scheme or schemes seem to offer the most hope for removing vinyl chloride from stack gases via chemical reaction. Particular attention will be paid to vinyl chloride conversion (especially when oxygen and nitrogen, eg air, are present) and to reaction product disposal (or use).

Reaction mechanisms will be studied to determine if other compounds might offer an advantageous reation.

Eventually, laboratory experiments will be set up to simulate vinyl chloride removal with the goal of 1 ppm maximum vinyl chloride level in mind.

Table 1 : Elements and Compounds which React with Vinyl Chloride According to Chem Abstracts

I. Elements	II. Inorganic Compounds
As	CF_3I
Cl_2	CO
F_2	C_2F_4
at. H	ClF
H_2	ClNO
Hg	Cl_2O
active N	$Fe(CO)_5$
at. Na	HBr
S	HCN
Se	HCl
Si-Cu mixt.	HClO
O_2	HF
O_3	HI
	H_2S
	KNH_2
	NF_3
	N_2F_2
	$NaHSO_3$
	$Ni(OH)_3$
	PCl_3
	PCl_5
	quartz
	SF_5OF
	SO_2Cl_2
	SO_3ClN
	$S_2O_5F_2$

Table 1 (continued)

II. Inorganic Compounds (continued)

$SeCl_4$

SiH_4

silanes

III. Organic Compounds

alkyl chlorocyclohexanes

amines

anisole

benzene

1,3-butadiene

C-56

2-chloro-2-methyl propane

chloroparaffins

cycloalkyl halides

cyclopentadiene

cyclopropyl

dicarboxylic acid chlorides

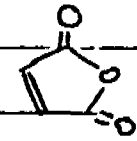
1,1-dichloroethane.

dihaloalkanes

1,2-ethanedithiol $HSCH_2CH_2SH$

ethanol

ethyl vinyl ether

maleic anhydride 

mercapto Ketones

2-methylcaptoethanol $CH_2SCH_2CH_2OH$

methyl mercaptan

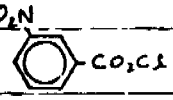
Table 1 (continued)

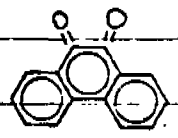
III. Organic Compounds (continued)

methyl phosphonous dichloride

2-methyl propane

methyl radicals

nitrobenzoyl chlorides 

oxalyl chloride ClCOCOCl 

9,10-phenanthrenequinone

phenol compds. $PhNO_2$ – $PhNH_2$

phtalimide derivs.

toluene

tetrachlorocyclopentadienone di-Me acetal

trifluoroethylene

IV. Organometallic Compounds

butyl lithium

chlorovinyl magnesium

dichlorodimethyl silane

ethyl aluminum chlorides $C_2H_5AlCl_2$, $(C_2H_5)_2AlCl$

methyl aluminum compds.

phenol magnesium bromide

(tert-butyl thio) sodium