

MAJOR OBJECTIVES

The major objectives of this research problem are:

- 1) To develop the required analytical instrumentation and techniques for pyrolyzing PVC resin, compounds, copolymers, and other polymers, and
- 2) To expand this technology into areas involving thermo-oxidation and combustion.

LIMITED OBJECTIVES

The objectives of this study were to study the combustion products from vinyl chloride monomer in joint work with personnel from Dow Chemical, Uniroyal and Borden Chemical. This task force is a part of the overall committee sponsored by the Manufacturing Chemists Association to investigate the burning of vinyl chloride monomer.

SUMMARY OF CONCLUSIONS

- A) Conflicting evidence exists on phosgene as a combustion product. Borden, Uniroyal and BFG have reported none present; Dow Chemical has reported the following levels of phosgene for the following conditions:

	<u>ppm (in air)</u>
diffusion flame	nil
premixed flame	10-200
VCM burning in an open dish	15-20
VCM burning in a ruptured tank	40

(All gas samples were obtained directly above the flame in each case)

- B) The following conclusions were derived from studies carried out at BFG:

- 1) When vinyl chloride is burned, 52% of the monomer unit is converted to HCl. This accounts for 89% of the available HCl; the remaining 11% was assumed lost on the combustion apparatus and adsorbed on the generated soot particles. In addition, a small portion of the VCM escaped combustion.

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- 2) A typical vinyl chloride flame releases 3-5% unoxidized carbon in the form of a light soot.
- 3) The ratio (weight/weight) of carbon dioxide to carbon monoxide in vinyl chloride combustion gases was found to be 5.81.
- 4) The overall combustion profile for vinyl chloride is:

<u>Combustion Products</u>	<u>Weight %</u>
HCl (determined)	52
HCl (assumed lost)	6
Carbon (as soot)	4
Carbon (as CO ₂)	30
Carbon (as CO)	8

- 5) The relative concentration of HCl, CO, CO₂ and phosgene (DOW's data) in a sample of air obtained directly above a vinyl chloride flame was:

<u>Component</u>	<u>ppm</u>	
	<u>Concentration</u>	<u>MAC</u>
HCl	27,000	5
CO	10,000	50
CO ₂	58,000	--
Phosgene*	40	0.5

- 6) Based on the Maximum Allowable Concentrations (MAC, above) of these combustion products, the overall toxicity from burning vinyl chloride is due to the gross amount of HCl in the combustion gases. The concentration of phosgene is 80X the MAC value, carbon monoxide is 200X and HCl is greater than 5000X the MAC value.

On the other hand, the toxicity may be due to the carbon monoxide content. This has been the case with the combustion gases from PVC which also contain a high level of HCl.

Animal testing would be required to differentiate the two situations.

* Value obtained by Dow for a ruptured tank fire.

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INTRODUCTION

In a previous report¹, the question of the presence of phosgene in the combustion gases from vinyl chloride monomer (VCM) was dealt with. At that time, it was reported that no phosgene (down to 10 ppm) could be detected when vinyl chloride was burned under diffusion flame conditions (no premixing of VCM and air). Three other laboratories have also investigated the "phosgene question" and have reported the following results:

Borden Chemical	- phosgene not detected
Uniroyal	- phosgene not detected
Dow Chemical	- not detected for VCM diffusion flame, 10-40 ppm detected for VCM burning in an open dish or in a ruptured tank (sampled immediately above the flame); 40-200 ppm detected for a premixed VCM flame

As a result of the Dow report, a number of additional experiments were carried out in an attempt to duplicate their work. The same combustion apparatus was used as previously described¹ except for the following modification. R. Daniels of Dow in a personal communication has reported that HCl (but not phosgene) is removed from combustion gases when the gases are directed through mossy zinc. The VCM combustion gases were treated in this manner and again analyzed for phosgene. Unfortunately, no phosgene could be detected.

From a toxicological standpoint, the amount of phosgene found by Dow is insignificant in view of the gross amount of HCl that is present.

HCl Determination

The combustion apparatus has been previously described¹ in detail. Briefly, it consists of a total combustion burner containing VCM and air lines, a chimney with an outlet at the top, an all glass trap for analyzing HCl or phosgene and an outlet line connected to a vacuum pump. Small vent holes were drilled into the base of the burner housing so that air could be drawn through the entire system.

For typical HCl determination, the apparatus was well seasoned with combustion products before any analyses were carried out. The decomposition gases were bubbled through 3 gas dispersion tubes (in parallel) into a standard sodium hydroxide solution. The off gases from this scrubber were directed into a silver nitrate solution in order to insure that a complete titration had taken place. A back titration of the sodium hydroxide solution with a standard HCl solution completed the analysis. The amount of HCl in the combustion gases was then related to the amount of VCM burned. As a result of this analysis, it was found that 52% of monomer by weight is converted to HCl.

¹ M.M.O'Hara, Part VIII, Status Report, 12/4/1969.

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Ash Content

Burning vinyl chloride has a characteristic cool, carbonaceous flame. It was of interest to determine the amount of carbon in terms of the amount of vinyl chloride consumed. Experiments were carried out in which the off gases from the vinyl chloride flame were directed through a piece of glass wool. This effectively trapped all of the unburned carbon from the flame.

The following table summarizes the results of two typical runs for two different burning rates. The results indicate that at a higher feed rate of vinyl chloride into the burner with a constant air supply, the amounts of carbon in the flame increase.

Total VCM Burned	4.00g	8.80g
Rate of VCM Consumption	0.133 g/min.	.088 g/min.
Amount Carbon Deposited	0.226 g	0.235 g
% Unburnt Carbon	5.5%	2.8%

Ratio of CO₂/CO

This important value was obtained by a gas chromatographic analysis of the off-gases from the VCM flame. A combination of columns (Porapak S, 6' x 1/4" and 5A Molecular Sieve, 1' x 1/4") enabled the complete separation of nitrogen, oxygen, CO₂, CO, VCM, and ethylene. The off-gases from the flame were sampled at two points in the combustion apparatus. One sample was taken at the top of the combustion chimney with no air flow through the system; the other was taken directly above the flame. G.C. analyses of these samples showed that the weight ratio of CO₂/CO was 16.5 for the first sample and 5.8 for the second. It was felt that the 16.5 ratio was too high and was not representative of the actual fire conditions. The conditions under which this sample (16.5 ratio) were taken were such that the combustion products were released to a confined area (no air stream to remove products from combustion chimney). The result of this was a secondary reaction involving the combustion of carbon monoxide...the extraordinarily high ratio of CO₂/CO.

The concentrations of CO, CO₂, H₂, and O₂ are presented in the following table, along with the appropriate response factors.

<u>Component</u>	<u>Response Factor</u>	<u>Weight %</u>
Oxygen	1.164	14.7
Carbon dioxide	0.906	5.8
Nitrogen	1.000	78.5
Carbon monoxide	0.977	1.0

An oxygen balance could not be calculated due to the loss of combustion water in the sampling apparatus.

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Unfortunately the HCl content of this air sample could not be calculated due to the poor resolution of this component on the gas chromatograph. This analysis nevertheless clearly defines the toxicity of the combustion gases from VCM. Assuming that Dow's phosgene data is correct, the concentration of this gas in the immediate vicinity of the flame* is 40 ppm or 80 times the accepted Maximum Allowable Concentration; the concentration of carbon monoxide near the flame is 10,000 ppm or 200 times the MAC value. Based on the amount of CO and CO₂ in the air sample, the concentration of HCl is estimated to be 27,000 ppm or 5400 times the MAC value.

Toxicity of Combustion Products

The toxicity of the combustion products from vinyl chloride might be expected to be due to the high content of HCl. However, an important piece of work should be interjected at this point. H.H.Cornish² has shown that the toxicity of the combustion products from poly (vinyl chloride) which also contain a high level of HCl are due not to this gas but rather due to carbon monoxide. This work showed a definite relationship between animal mortality (mice, rats, guinea pigs, rabbits and monkeys) and the concentration of blood carboxyhemoglobin.

A similar situation may be in effect for the combustion products from vinyl chloride although the Maximum Allowable Concentration Values indicate that HCl is the greatest contributor to the overall toxicity.

Additional Studies

The analytical results from this study have been extended to actual fire conditions involving VCM. L.B.Crider has initiated a computer study in which the concentration of HCl and carbon monoxide are described in terms of:

- 1) distance from the fire
- 2) type of geographic terrain where fire occurs
- 3) wind conditions, and
- 4) temperature conditions

This results of the study will be made available to MCA as a guide for dealing with future VCM fires.

* Ruptured vessel fire

² H.H. Cornish, Arch. Environ. Health, Vol. 19, July 1969, p. 15-21.

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