RESEARCH STUDY ON BIS(CHLOROMETHYL)ETHER FORMATION AND DETECTION IN SELECTED WORK ENVIRONMENTS

C.C. Yao, Ph.D.
G.C. Miller, M.S.P.H.

The Bendix Corporation
Launch Support Division
Cocoa Beach, Florida 32931

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NIOSH Project Officers: Troy Marceleno
Melvin Cassady
James H. Jones
Richard E. Kupel

Principal Investigators: C.C. Yao
G.C. Miller

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16. Abstract (Limit: 200 words)

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ABSTRACT

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I. SUMMARY

A study of the mechanisms of bis(chloromethyl) ether (BCME) formation, and a survey of its presence in selected industrial environments, sponsored by the National Institute for Occupational Safety and Health, were carried out by the Bendix Launch Support Division, Special Projects Group. This report consists of two parts.

Part I presents the results of the kinetic study of BCME formation in gas phase and in polar and nonpolar condensed phases (methylene chloride and carbon tetrachloride, respectively). The reaction mechanisms were postulated. Some rate equations were integrated. Activation energies for BCME formation in gas phase, carbon tetrachloride, and methylene chloride were found to be 19.8, 18.9, and 5.24 Kcal. per mole, respectively. Obviously, the BCME formation is greatly facilitated in the polar medium. Also included in this part are the evaluation of the BCME trapping techniques and analytical procedures.

Part II presents the results of the on-site survey of two textile finishing plants, one fertilizer plant, two dye manufacturing plants, two foundries, and one hospital procedure resin production laboratory. No detectable BCME was found in any of the industries visited (detectable limit, 0.1 ppb). The highest amounts of formaldehyde (6 ppm) were found in foundry and dye manufacturing plants. Only 1 to 2 ppm were found in other industries (detectable limit, 0.1 to 1 ppm). The highest total chloride (21 ppm) was found in a fertilizer plant. Only 1 to 3 ppm, if any at all, were found in other industries (detectable limit for total chloride, 0.1 to 1 ppm; detectable limit for hydrogen chloride, 1 ppm). This survey task was conducted by a survey team led by Mr. Gordon Miller, and the analyses were performed in the mobile laboratory, except those involving mass spectrometry.

II. CONCLUSIONS

A. Part I

1. The activation energy for the formation of BCME in the gas phase was found to be 19.8 Kcal per mole. The reaction rate decreases drastically as temperature is lowered. Thus, the BCME formation from formaldehyde and hydrogen chloride in the gas phase will be extremely slow at ambient temperatures.

2. The activation energy for the formation of BCME in the nonpolar condensed phase (carbon tetrachloride) was found to be 18.9 Kcal per mole. The lowering of activation energy due to solvation, if it exists, is insignificant. The reaction temperature effect, although not as great as in the gas phase, is still considerable. Thus, the rate of BCME formation from form aldehyde and hydrogen chloride in the nonpolar condensed phase (carbon tetrachloride) at ambient temperature will be still relatively slow.

3. The activation energy for the formation of BCME in the polar phase (methylene chloride) was found to be 5.24 Kcal per mole. The energy barrier is much lower and the reaction can proceed with ease. The temperature effect on reaction is greatly reduced. In other words, the rate is less sensitive to temperature changes.

4. The formation of BCME in the gas phase is unlikely to be spontaneous at ambient condition. The extent of BCME formation in the

nonpolar phase is still small. The formation of BCME in the polar phase is, however, definitely favored.

5. BCME undergoes thermal and chemical decompositions. A 12.9 percent decomposition was noted when it was kept at 91° C for 18.3 hours. A 20 percent decomposition was noted or "for 15 minutes" in the presence of strong acid and at 80°C.

6. BCME can be formed in aqueous medium from formaldehyde and chlorides. Its yield increases greatly on addition of chlorosulfonic acid. The extent of its subsequent hydrolysis depends on its concentration, the temperature, and residence time. The yields of BCME in aqueous medium vary inversely with reaction temperature, indicating a greater decomposition at higher temperatures.

7. BCME formation shows a third-order kinetics; second-order with respect to formaldehyde.

8. Moisture plays an important part in the formation of BCME in the industrial environment. It is postulated that its role is not in the sense of direct participation, but rather in providing a favorable reaction medium in the form of water clusters, droplets, and adsorbed films on airborne particulates and on stationary surfaces.

B. Part II

From the data developed, several conclusions can be reached about the formation of BCME in the work environment.

- The formation of BCME does not occur regularly or in sufficient quantities to be detected at the low tenths of a ppb level in the environments studied under the conditions found.

- The potential formation cannot be entirely ruled out because of the known formation reactions of BCME (Part I of this report), and the known presence of formation components in the industrial environments studied.

- Formation potential for BCME may be influenced by environmental parameters such as temperature, humidity, etc., which could affect the formation conditions.

- Further study on detection methods is needed to allow relatively interference-free BCME determinations.

III. RECOMMENDATIONS

A. Part I

The carcinogenicity of BCME has been established beyond doubt (see Section IV). In spite of the fact that the BCME formation in gas phase is negligible at best, and its formation in nonpolar condensed phase is very slow, its formation in the polar, including aqueous, media proceeds with facility, and its threat to occupational health is real and serious. Whenever formaldehyde and chlorides are present in quantity, the formation of BCME cannot be discounted, either in the bulk of solutions, in moisture droplets, in adsorbed film on airborne particulates, or in condensed covering of solid surfaces on the ground.

It is therefore recommended that effort must be made to avoid the coexistence of formaldehyde and chlorides in the same confinement. For industrial processes utilizing both these components, substitutes for either of the two have to be found. This is the way, and the only way, that the healthy life of numerous productive workers can be protected.

B. Part II

Overall, while no BCME was found, its formation cannot be completely discounted in the work environment. Further study may be needed to further quantitate and qualitate formation potentials to ensure that every work environment is free of BCME even at the lowest detectable levels.

IV. INTRODUCTION

alpha-Haloalkyl ethers are highly reactive and widely used as intermediates in laboratories and industries.[1] Among them, the bis(chloromethyl) ether (BCME) was repeatedly identified as a potent carcinogen by several renowned researchers. On application of a dose of 2 mg BCME three times weekly on mouse skin, the appearance of tumor was noted within 161 days. [2] Subcutaneous injection of a single dose of BCME (12 ml per kg) into newborn mice induced lung adenomas within 6 months. [3] Chronic inhalation of 1 ppm BCME by mice resulted in an increase in incidence of pulmonary adenomas. [4] Inhalation by rats of 0.1 ppm BCME produced squamous cell carcinomas of the lung and esthesioneuroepitheliomas of the olfactory epithelium. [5] About an eight-times increased incidence of lung cancer occurred among men exposed to chloromethyl methyl ether (CMME), which, in general, contains 1 to 7 percent BCME.[6] CMME, however, has been found inactive in mouse skin tests. These observations seem to establish beyond doubt that BCME is an occupational hazard.

Since BCME has been prepared routinely in research laboratories and in various industries from paraformaldehyde and hydrochloric acid, [2,7,8] and formaldehyde, hydrogen chloride, and metal chlorides are common chemicals, the formation of BCME in the workplace atmosphere was inferred. In a study conducted by the National Institute for Occupational Safety and Health, trace amounts of BCME were indeed found in some cases in the textile-finishing process areas where formaldehyde was used. [9] Evidence of BCME formation in aqueous solution was found by NMR spectrum in trioxane (as formaldehyde source), deuterochloric acid, and heavy water [10] as a simulated textile-finishing solution.

However, results from studies in several industrial laboratories regarding the BCME formation from formaldehyde and chlorides are varied and sometimes appear contradictory: First, it was announced by Rohm and Haas [11] that BCME was formed spontaneously from formaldehyde and hydrogen chloride in parts-per-million range in humid air, and that a steady state was reached in less than 1 minute. Then, Kallos and Solomon [12] of Dow Chemical found that at ambient temperature and relative humidity, BCME is not formed in detectable amount (0.1 ppb) from formaldehyde and hydrogen chloride up to 200 ppm. At concentrations above 500 ppm, only low ppb levels of BCME were detected. The steady state was not attained at less than 18 hours. The reaction rate was independent of the humidity of the environment.

Later, experimental results from Frankel et al, of Rohm and Haas [13] indicated that BCME formation was exponentially related to the reactant concentrations. The reaction was indifferent to the reactor surface character; its rate was slow, at 0.01 mole percent, based on hydrogen chloride concentration. The yield was extremely nonreproducible under 100 percent relative humidity, and consistently lower in dry atmosphere, but showed no significant difference at either 40 percent relative humidity or ambient humidity. The reaction was found also insensitive to temperature at 40° C or ambient temperature.

Further studies in the laboratories of Dow Chemical [14] showed that BCME was not observed from the reaction of aqueous hydrochloric acid and formaldehyde at concentrations up to 2,000 ppm at ambient temperature for 18 hours (detection limits were 9 ppb in aqueous phase, and 1 ppb in gas phase above the reaction mixture). They concluded that, based on their kinetic data, BCME cannot be present at even much lower levels than 9 ppb in aqueous

solution. They further stated that the rate of hydrolysis of BCME in humid air (water content 2.6 percent) ranged between 0.0016 to 0.00047 minute-1 had $t_{\frac{1}{2}}$ greater than 25 hours and was faster in a ferric-oxide-coated saran bag than in a glass reactor.

The purpose of this contract is twofold: First, to understand and establish reaction mechanisms of BCME formation from formaldehyde and chlorides and their parameters, and to evaluate the sampling techniques and analytical procedures; and, second, to detect the presence and determine the level of BCME if it is actually formed in selected work environments.

PART I

KINETICS AND MECHANISMS

V. POSSIBLE REACTION MECHANISMS FOR BCME FORMATION

The formation of BCME from formaldehyde and hydrogen chloride in condensed phase was well known, first described in 1887. [7] Its reaction mechanism can be postulated in more than one way. For the sake of completeness, the reaction can be classified in terms of three different media: the vapor phase reactions, the polar and nonpolar condensed phase reactions, and heterogeneous reactions (gas-liquid, gas-solid, and liquid-solid systems). At the present time, homogeneous reactions only are considered, and their reaction routes are shown in the following flow charts (shown as Figures 1, 2, and 3 on the following pages) according to which of the three components, water, formaldehyde, or hydrogen chloride, is present in excess. This is not only due to the possible existence of such actual conditions, but also for the simplification and convenience of kinetic treatment. It does not imply, however, that all of the ramifications can actually occur, nor that all the possibilities are included. The final identification of reaction mechanisms has to be decided by experimental evidence.

A. Vapor Phase Reactions

In the vapor phase reaction, the reacting mode would be molecular and homogeneous in nature. At very dry condition (Path A), the water concentration is much less than that of hydrogen chloride. The reacting species might be chloromethyl alcohol ($ClCH_2OH$). Although it has been frequently postulated as a reacting intermediate in chloromethylation process, its physical existence has never been established until recently by low-temperature NMR spectroscopy. [15] The collapse of the 4-centered transition state of two chloromethanol molecules by the shifting of the bonding electrons, as indicated by the curved arrows

would result in BCME formation. On the other hand, when the hydrogen chloride concentration is much less than that of water (Path C), the reacting species might be methylene glycol ($HOCH_2OH$). The collapse of the 4-centered transition state of two methylene glycol molecules by the shifting of the bonding electrons, as indicated by the curved arrows, would result in the formation of bishydroxymethyl ether, which in turn, again forms 4-centered transition states, either consecutively or simultaneously, or both, with two hydrogen chloride molecules. The subsequent collapse of each of these 4-centered transition states would displace the hydroxyl groups with chlorine atoms at α-carbon atoms to form BCME. If formaldehyde's presence is in great predominance (Path B), it is conceivable that a 4-centered transition state might also be involved, which, with the aid of hydrogen chloride, collapses to form chloromethoxymethanol. The formation and subsequent collapse of the next 4-centered transition state of the latter with hydrogen chloride finally afford the BCME. Naturally, this is only a hypothetical case listed here for the sake of completeness, following the same pattern of thought. In reality, formaldehyde under this condition would have polymerized to linear and cyclic polymers long before anything else could happen.

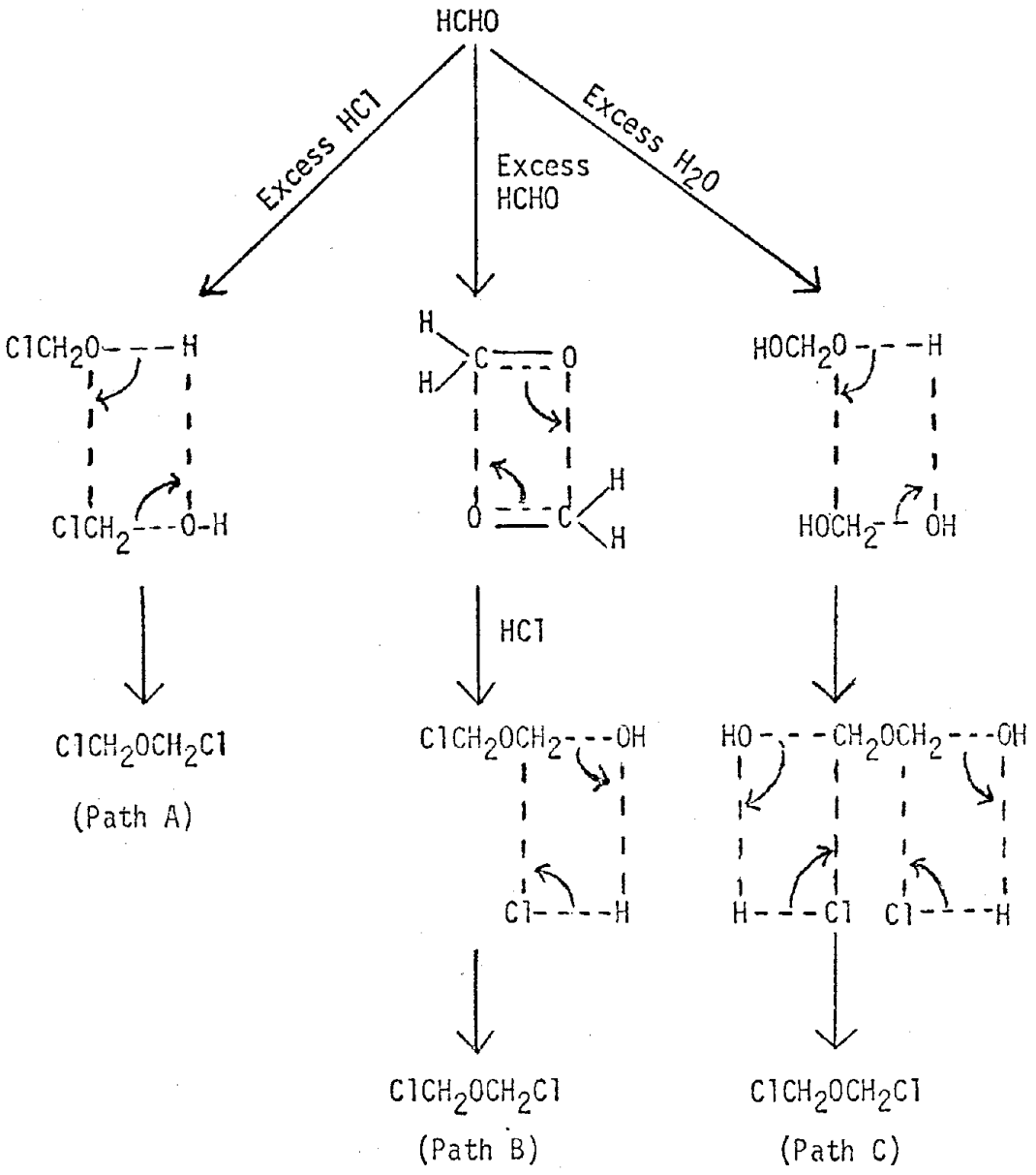


FIGURE 1. VAPOR PHASE

B. Nonpolar Condensed Phase Reactions

In nonpolar condensed phases, the reaction would proceed either by way of molecular mode or through SN2 replacement. Here again, three paths of reaction are postulated: In the Path A, chloromethanol is postulated as the intermediate, owing to the excess condition of hydrogen chloride. In the Path B, the reaction is visualized as proceeding through a polarized formaldehyde dimer transition state, owing to the excess condition of formaldehyde and possible tendency of solvation. Subsequent substitutions consummate the reaction. Naturally, this is only a hypothetical case listed here for the sake of completeness, following the same pattern of thought. In reality, as it was found out later in this study, formaldehyde under this condition would have polymerized to linear and cyclic pclymers long before anything else could happen. In the Patch C, methylene glycol is postulated as the intermediate, owing to the excess condition of water. The subsequent displacements of hydroxyl groups by chlorine atoms or chlorides can take place either consecutively or simultaneously, or both

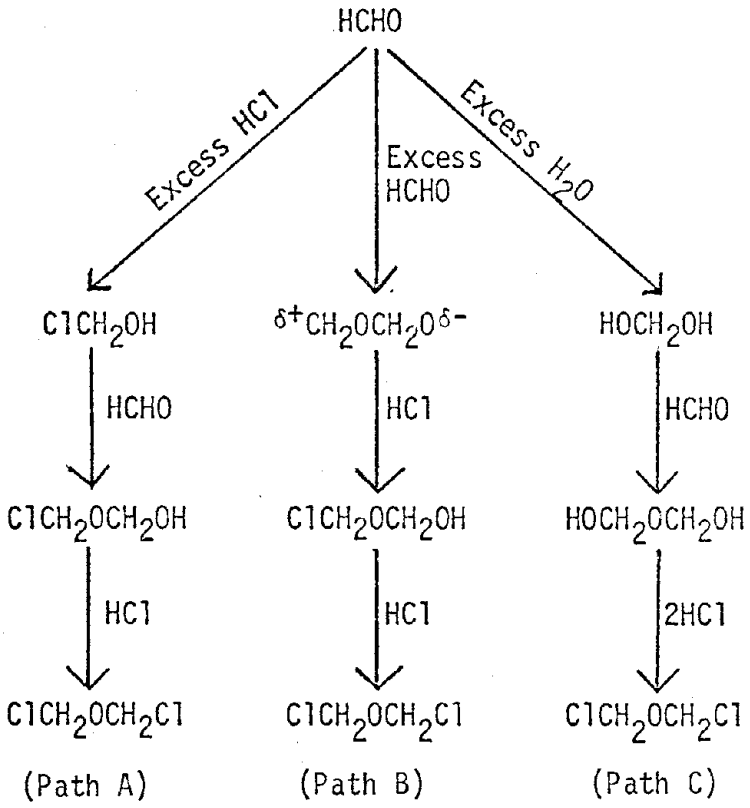


FIGURE 2. NONPOLAR MEDIA

C. Polar Condensed Phase Reactions

In strongly polar media, the reaction could proceed through SN1 type of replacement. Here again, three paths of reaction are postulated: In the Path A, chloromethanol is postulated as the intermediate, owing to the excess condition of hydrogen chloride. Chloromethoxymethyl carbonium ions are then postulated to exist on the basis of the strongly polar medium and favorable resonance charge distribution. The unimolecular nucleophilic substitution consummates the reaction. In the Path B, the reaction is visualized as proceeding through a polarized formaldehyde dimer transition state, owing to the excess condition of formaldehyde and the highly polar medium. The subsequent nucleophilic substitutions consummate the reaction. Naturally, this is a hypothetical case, listed here only for the sake of completeness, following the same pattern of thought. In reality, as it was found out later, the competitive polymerization processes of formaldehyde would prevail. In the Path C, methylene glycol is postulated as the intermediate, owing to the excess condition of water. The subsequent displacements of hydroxyl groups by chlorides can take place either consecutively or simultaneously, or both.

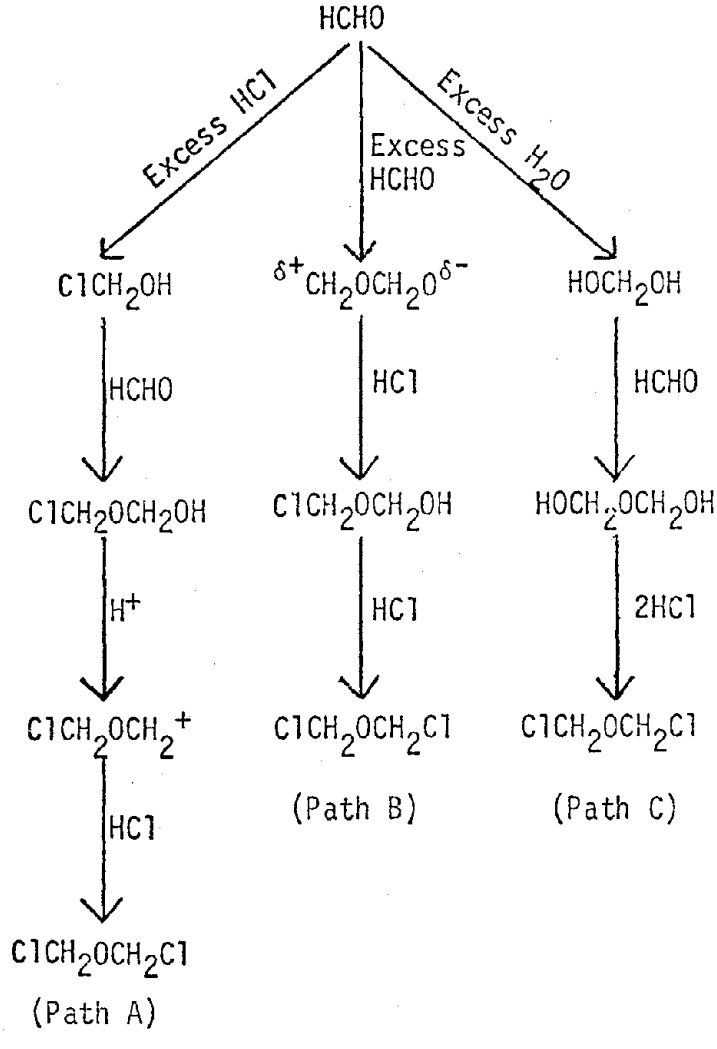


FIGURE 3. POLAR MEDIA

VI. INTEGRATED KINETIC RATE EQUATIONS

In view of the multiplicity of reaction schemes and the variety of existing experimental data, and to resolve the selection and elimination process, kinetics of the reaction in gaseous as well as in condensed phases were studied. The final identification of reaction mechanisms from numerous variations and the establishment of respective rate equations have to be decided by experimental evidences and curve-fitting results. Some but, of necessity, not all of the rate equations were integrated. Among them are the following:

A. Via Chloromethyl Alcohol Intermediate and 4-Center Transition State

$$HCHO + HCl \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ClCH_2OH$$

$$2ClCH_2OH \xrightarrow{k_2} ClCH_2OCH_2Cl + H_2O$$

$$\frac{d[BCME]}{dt} = -\frac{d[ClCH_2OH]}{2dt} = k_2[ClCH_2OH]^2$$

$$= -\frac{K_e}{2}\frac{d[HCHO][HCl]}{dt} = k_2K_e^2[HCHO]^2[HCl]^2$$

$$\text{here } K_e = \frac{[ClCH_2OH]}{[HCl][HCHO]}$$

$$-\frac{d[HCHO][HCl]}{dt} = 2k_2K_e[HCHO]^2[HCl]^2$$

When HCl is in excess,

$$-\frac{d[HCHO]}{dt} = k_{obs.}[HCHO]^2$$

$$-\int\frac{d[HCHO]}{[HCHO]^2} = \int k_{obs.}\,dt$$

$$\frac{1}{[HCHO]} = k_{obs.}t + \frac{1}{[HCHO]_o} \qquad \text{(Eq. 1)}$$

Therefore, the reaction is of a pseudo second-order kinetics with respect to formaldehyde.

When HCHO and HCl are at equivalent concentrations, x.

$$-\frac{dx^2}{dt} = 2k_2K_ex^4$$

$$-2x\frac{dx}{dt} = 2k_2K_ex^4$$

$$-\frac{dx}{dt} = k_2K_ex^3$$

$$-\int\frac{dx}{x3} = k_2K_e\int dt$$

$$\frac{1}{x^2} = k_2K_et + \frac{1}{x_o^2} \qquad \text{(Eq. 2)}$$

Therefore, the reaction is of third-order kinetics.

B. Via Formaldehyde Dimer and 4-Center Transition State

$$2HCHO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \begin{matrix} H_2C\cdots O \\ \vdots \quad \vdots \\ O\cdots CH_2 \end{matrix} \quad \text{(T.S.)}$$

$$\begin{matrix} H_2C\cdots O \\ \vdots \quad \vdots \\ O\cdots CH_2 \end{matrix} + 2HCl \xrightarrow{k_2} ClCH_2OCH_2Cl + H_2O \quad \text{(BCME)}$$

$$\frac{d[BCME]}{dt} = -\frac{d[HCl]}{2dt} = k_2[T.S.][HCl]^2$$

$$= k_2K_e[HCHO]^2[HCl]^2$$

When HCHO is in excess,

$$-\frac{d[HCl]}{dt} = k_{obs.}[HCl]^2$$

$$-\int\frac{d[HCl]}{[HCl]^2} = k_{obs.}\int dt$$

$$\frac{1}{[HCl]} = k_{obs.}t + \frac{1}{[HCl]_o} \qquad \text{(Eq. 3)}$$

Therefore, the reaction is of pseudo second-order kinetics with respect to hydrogen chloride.

C. Via $HOCH_2OH$ and 4-Center Transition State

$$HCHO + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HOCH_2OH$$

$$2HOCH_2OH \xrightarrow{k_2} HOCH_2OCH_2OH + H_2O$$

$$HOCH_2OCH_2OH + 2HCl \xrightarrow{k_3} ClCH_2OCH_2Cl + 2H_2O$$

$$\frac{d[BCME]}{dt} = k_3[HOCH_2OCH_2OH][HCl]^2$$

$$\frac{d[HOCH_2OCH_2OH]}{dt} = -k_3[HOCH_2OCH_2OH][HCl]^2 + k_2[HOCH_2OH]^2$$

Evidently, a condition of $k_3 > k_2$ has to be assumed.

$$\frac{d[BCME]}{dt} = -\frac{d[HOCH_2OCH_2OH]}{dt} = -\frac{d[HOCH_2OH]}{2dt} = k_2[HOCH_2OH]^2$$

$$-\frac{K_e d[HCHO][H_2O]}{2dt} = k_2K_e^2[HCHO]^2[H_2O]^2$$

$$-\frac{d[HCHO][H_2O]}{dt} = 2k_2K_e[HCHO]^2[H_2O]^2$$

When H_2O is in excess, Eq. 1 will result.

When HCHO and H_2O are at equivalent concentration, Eq. 2 will result.

D. Condensed Phase Reaction

$$HCHO + HCl \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ClCH_2OH$$

$$ClCH_2OH + HCHO \xrightarrow{k_2} ClCH_2OCH_2OH$$

$$ClCH_2OCH_2OH + HCl \xrightarrow{k_3} ClCH_2OCH_2Cl + H_2O$$

$$\frac{d[BCME]}{dt} = k_3[ClCH_2OCH_2OH][HCl]$$

when $k_2 < k_3$,

$$\frac{d[BCME]}{dt} = \frac{d[ClCH_2OCH_2OH]}{dt} = -\frac{d[ClCH_2OH]}{dt}$$

$$-\frac{d[ClCH_2OH]}{dt} = k_2[ClCH_2OH][HCHO]$$

$$-K\frac{d[HCHO][HCl]}{dt} = k_2K[HCHO]^2[HCl]$$

when HCHO and HCl are at equivalent concentration x,

$$-\frac{dx^2}{dt} = k_2x^3$$

$$-2x\frac{dx}{dt} = k_2x^3$$

$$-2\frac{dx}{dt} = k_2x^2$$

$$-\int\frac{dx}{x^2} = \frac{k_2}{2}d\int dt$$

$$\frac{1}{x} = \frac{k_2}{2}t + \frac{1}{x_o} \qquad \text{(Eq. 4)}$$

when HCl is in excess and HCHO concentration is x,

$$-\frac{dx}{dt} = k_2 x^2$$

$$-\int\frac{dx}{x^2} = k_2\int dt$$

$$\frac{1}{x} = k_2 t + \frac{1}{x_o} \qquad \text{(Eq. 5)}$$

VII. BCME FORMATION IN GAS PHASE

The study of gas phase reaction kinetics was intended to be carried out in plastic bags as it was done in many laboratories in their study of BCME formation, taking the advantage of its simplicity and convenience. It was soon found that the permeation rate of the Tedlar bag was so great, particularly at elevated temperatures, it rendered the Tedlar bag unsuitable for kinetic measurements. The permeation of formaldehyde, as measured by chromatograph peak heights of aliquot samples from the bag (which contained 0.037 HCHO in 10 l. N_2) versus time, is shown in Figure 4. The experiments were therefore carried out in a glass apparatus enclosed in a constant-temperature chamber, the details of which are described in Section XVIII, Experimental.

Gaseous formaldehyde polymerizes readily. It was found in this laboratory that at temperatures above 80° C the formaldehyde will exist in gaseous state. Thus, the experiments in gas phase reactions were all conducted above 80° C. The reaction kinetics were followed by the rate of disappearance of formaldehyde because it was twice as fast as that of the formation of BCME and, therefore, easier to measure.

The kinetic measurements are tabulated in Tables 1, 2, and 3. The corresponding plots are shown in Figures 5, 6, and 7. The applicable integrated rate equation is therefore Eq. 2. Therefore, the reaction is of third order kinetics, second-order with respect to formaldehyde and first-order with respect to hydrogen chloride, based on the stepwise reaction mechanism proposed in Section VI A. The data and the graph for the Arrhenius plot are shown in Table 4 and Figure 8.

The slopes of all the graphs were determined by the least square treatment. All graphs were drawn by the linear regression method. All the rate constants were expressed in terms of milliliter, millimole, and minute by making use of the experimentally determined conversion factor. The activation energy for the BCME formation from gaseous formaldehyde and hydrogen chloride calculated from the Arrhenius plot is 19.8 Kcal per mole. It represents a relatively large energy barrier that the reactant molecules must overcome before they can take part in the reaction process to yield BCME as the product. Furthermore, it is obvious from the steepness of the Arrhenius plot that, as the temperature decreases, the rate of the formation of BCME decreases logarithmically and very fast. Therefore, the formation of BCME from the formaldehyde and hydrogen chloride in the gas phase at ambient temperature will be extremely slow, if it forms at all. The calculated rate constant for gas phase reaction at 25° C is 10.39 $\mu l^2/\mu mole^2/min$. In other words, it is 200 times slower than the reaction at 81° C. Just a word of caution here: Do not compare this rate constant for gas phase reaction with those for nonpolar and polar phases. They are of different reaction mechanisms and in different units.

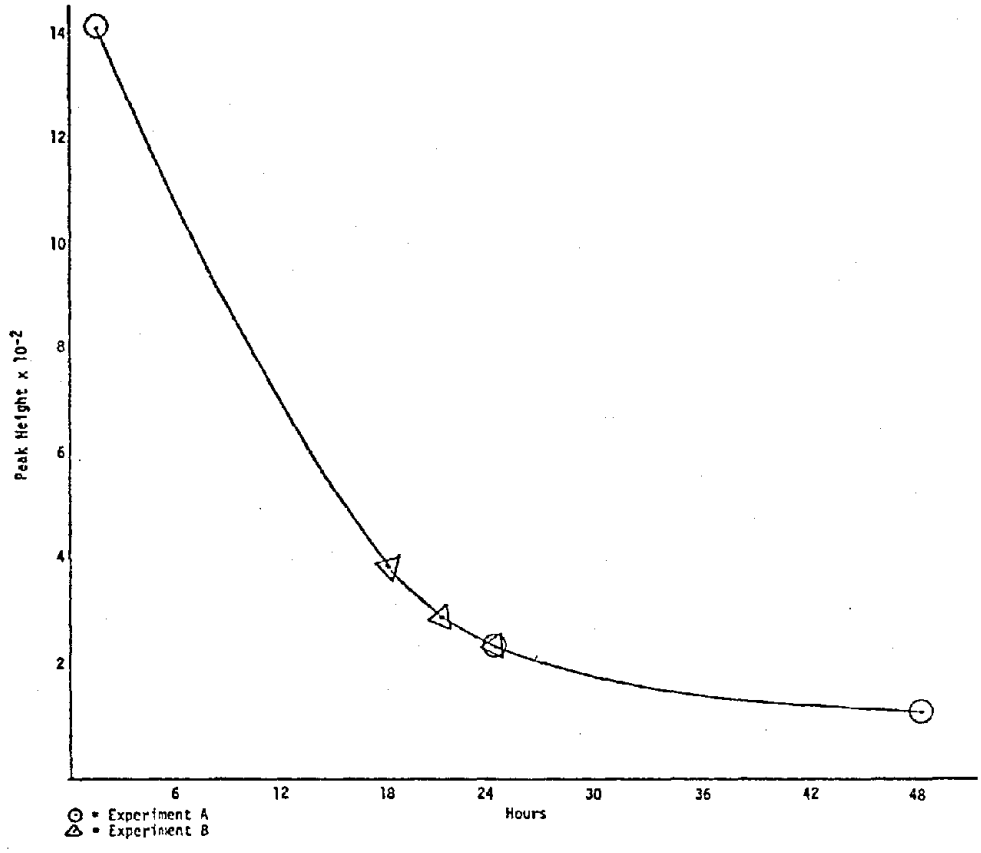


FIGURE 4. PERMEATION OF FORMALDEHYDE AT 94° C THROUGH TEDLAR BAG (0.037 mole HCHO in 10 l. N_2)

TABLE 1

KINETIC MEASUREMENTS OF FORMATION OF BCME IN GAS PHASE (81° C)

(HCHO/HCl = 1:1; 0.01666 mole each; diluent = N_2; temperature = 81° C)

Time (min.)	Sample Size (μℓ)	HCHO Peak Height (1μℓ)	1/(Peak Height)^2	Calibration
24	100	0.844 Div.	1.4038	1 μg = 29.6 Div.
81	100	0.800	1.5625	
168	100	0.736	1.8461	
210	100	0.732	1.8663	

Observed rate constant k = 2.088 x 10^3 $\mu\ell^2/\mu mole^2/min.$

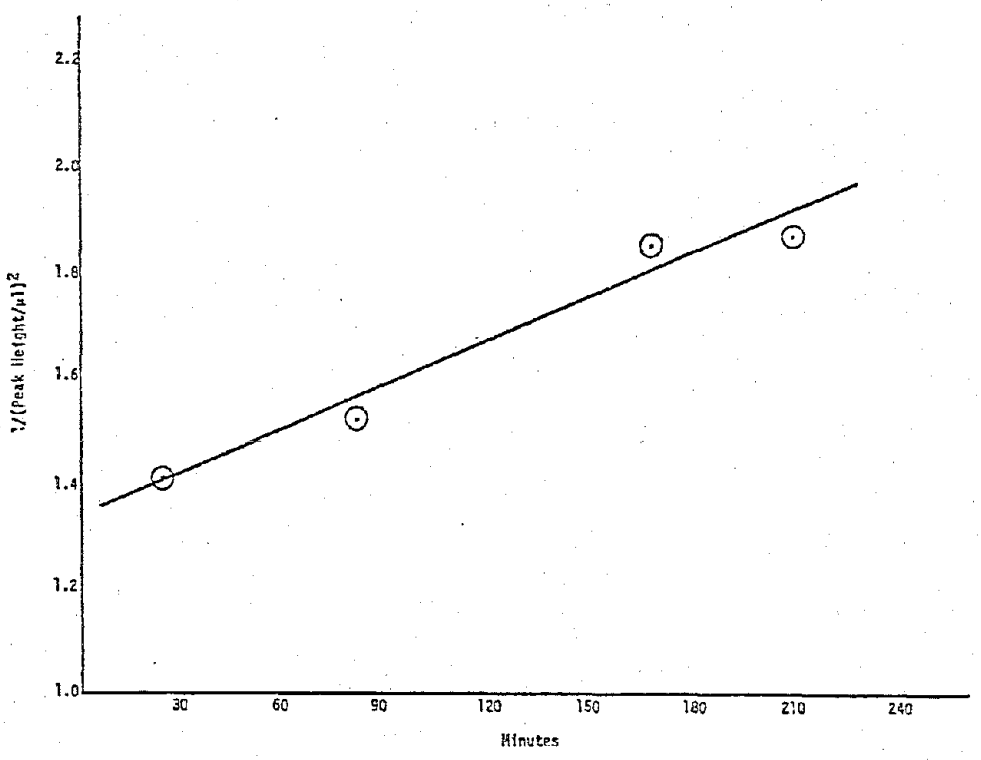


FIGURE 5. KINETIC PLOT FOR BCME FORMATION IN GAS PHASE AT 81° C

TABLE 2

KINETIC MEASUREMENTS OF FORMATION OF BCME IN GAS PHASE (94° C)

(HCHO/HCl = 1:1; 0.01855 mole each; diluent = N_2; temperature = 94° C)

Time (min.)	Sample Size (μℓ)	HCHO Peak Height (1μℓ)	1/(Peak Height)^2	Calibration
20	100	0.900	1.2345	1 μg = 28.35 Div.
36	100	0.900	1.2345	
96	100	0.880	1.2913	
165	100	0.768	1.6954	
273	100	0.636	2.4722	

Observed rate constant k = 4.869 x 10^3 $\mu\ell^2/\mu mole^2/min.$

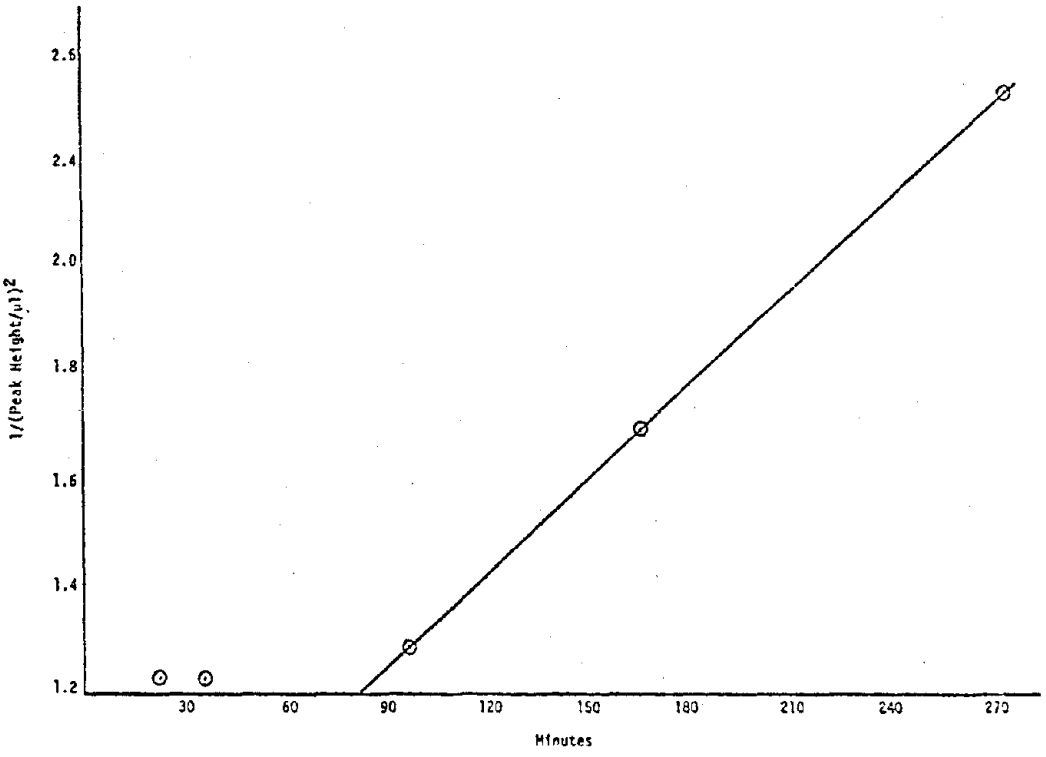


FIGURE 6. KINETIC PLOT FOR BCME FORMATION IN GAS PHASE AT 94° C

TABLE 3

KINETIC MEASUREMENTS OF FORMATION OF BCME IN GAS PHASE (96° C)

(HCHO/HCl = 1:1; 0.01673 mole each; diluent = N_2; temperature = 96° C)

Time (min.)	Sample Size (μℓ)	HCHO Peak Height (1μ)	1/(Peak Height)^2	Calibration
6	100	0.800	1.5625	1 μg = 30.3 Div.
78	100	0.528	3.5870	
138	100	0.486	4.2338	
180	100	0.484	4.2688	
411	100	0.368	7.3842	
481	100	0.398	6.3130	
531	100	0.360	7.7160	

Rate constant k = 7.229 x 10^3 $\mu\ell^2/\mu mole^2/min.$

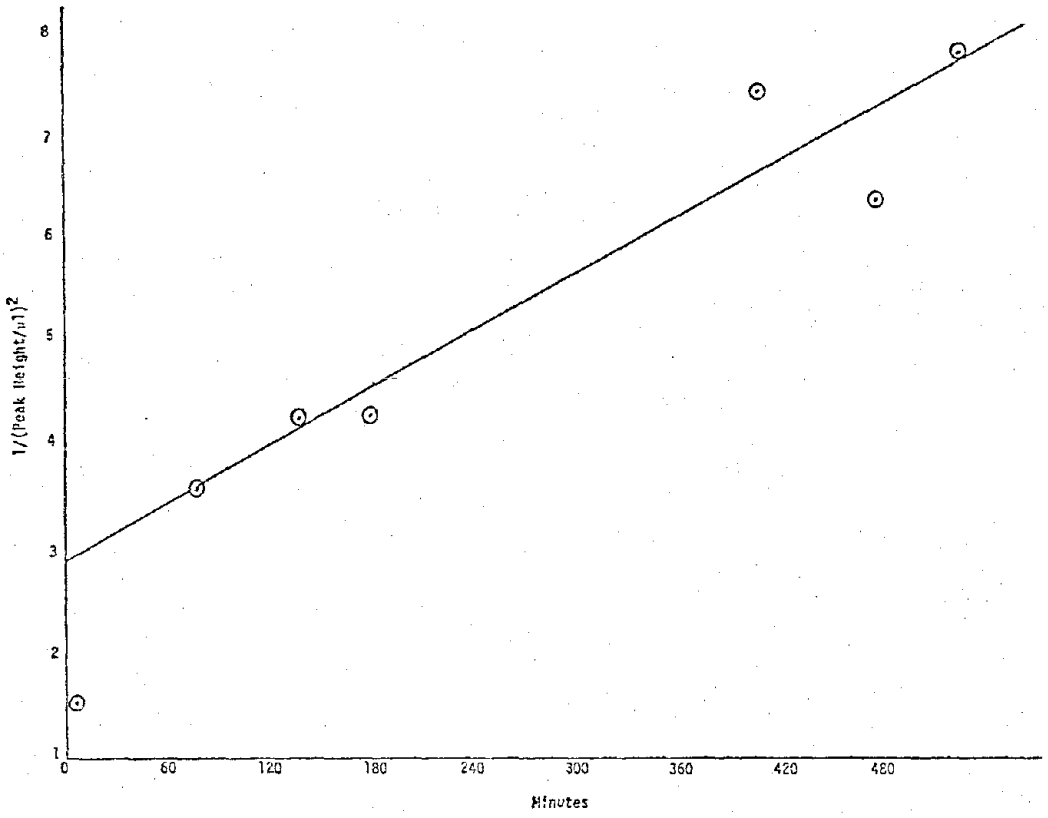


FIGURE 7. KINETIC PLOT FOR BCME FORMATION IN GAS PHASE AT 96° C

TABLE 4

RATE CONSTANTS FOR BCME FORMATION IN GAS PHASE

Media	HCHO/HCl	Temperature (° C)	1/T	$k(\mu\ell^2/\mu mole^2/min.)$	log k
GN_2	1	81.0	0.002825	2.088×10^3	3.3197
GN_2	1	94.0	0.002725	4.869×10^3	3.6874
GN_2	1	96.0	0.002710	7.229×10^3	3.8591

$E_{act.}$ = 19.8 Kcal/mole

$k_{25° C}$ (calculated) = 10.39 $\mu\ell^2/\mu mole^2/min.$

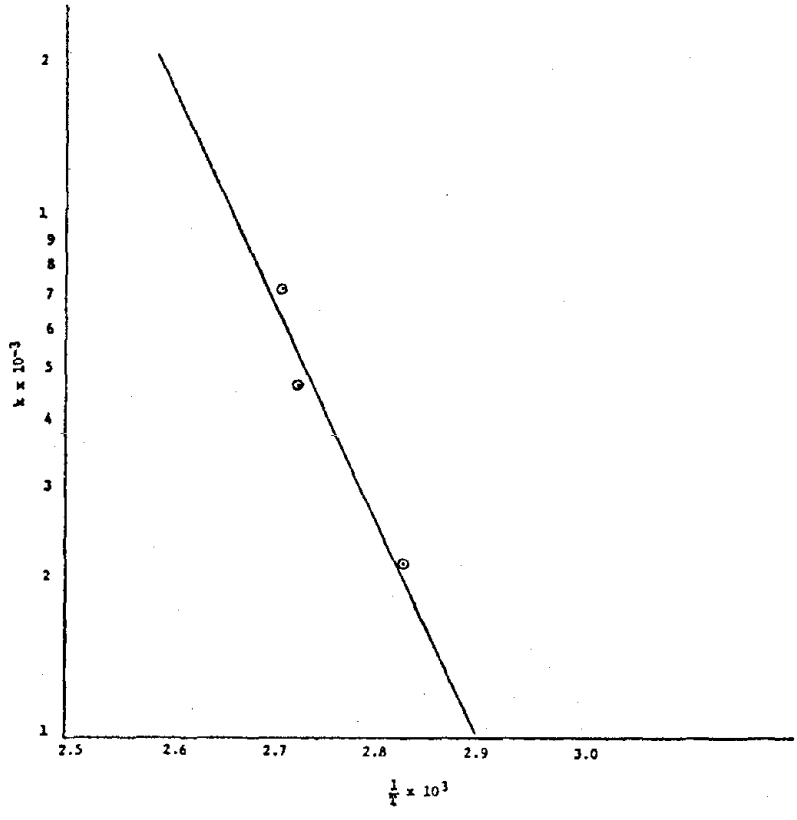


FIGURE 8. ARRHENIUS PLOT FOR BCME FORMATION IN GAS PHASE

VIII. BCME FORMATION IN NONPOLAR CONDENSED PHASE

Carbon tetrachloride was selected as a representative of nonpolar condensed media. The solubility of formaldehyde in carbon tetrachloride is naturally limited. At 0° C and concentrations above 59.7 μmole/ml, the formaldehyde will polymerize and precipitate as paraformaldehyde. Thus, the experiments of BCME formation in carbon tetrachloride were conducted at temperatures above 0° C when higher concentrations were used. Their respective concentrations of saturation at the selected temperatures, however, were not determined. No polymerizations of formaldehyde were encountered at the concentrations actually used at 9.8° C, 19.7° C, and 40° C. The apparatus used in the study of BCME formation in the condensed phases is described in Section XVIII, Experimental. The reaction kinetics were followed by the rate of disappearance of formaldehyde, taking advantage of its being twice as fast as that of the formation of BCME and, therefore, easier to measure at the dilution of the experiment.

The carbon tetrachloride solutions of formaldehyde and of hydrogen chloride were prepared separately and their concentrations determined. These two solutions were cooled to the reaction temperature and then mixed in the reactor, which was immersed in a constant-temperature bath. The method of mixing of these solutions is crucial to keeping the formaldehyde in solution. When the formaldehyde solution was poured into the hydrogen chloride solution with fast stirring, no polymerization of formaldehyde and precipitation of paraformaldehyde occurred. Reversed mode of addition, however, resulted in instant polymerization and precipitation. This phenomenon shows dramatically the dynamic equilibrium of formaldehyde, hydrogen chloride, and chloromethanol.

The kinetic measurements and experimental conditions are tabulated in Tables 5, 6, and 7. The corresponding plots are shown in Figures 9, 10, and 11. These experiments were conducted with excess hydrogen chloride. The applicable integrated rate equation is therefore Eq. 5. Therefore, the reaction is second-order with respect to formaldehyde with HCl in 5-fold excess. The data and the graph for the Arrhenius plot are shown in Table 8 and Figure 12, respectively.

The slopes of all the graphs were determined by the least square treatment. All graphs were drawn by the linear regression method. All the rate constants were expressed in terms of milliliter, millimole, and minute by making use of the experimentally determined conversion factor. The activation energy for the BCME formation in the nonpolar condensed phase, calculated from the Arrhenius plot, is 18.9 Kcal per mole, surprisingly similar in magnitude to that for the BCME formation in the gas phase.

The original purpose of the study of BCME formation in the nonpolar condensed phase was to provide a simulated gas phase reaction, in case difficulties were encountered in the actual gas phase studies, so that some information could be deduced pertaining to the molecular reactions. The similar magnitudes of activation energies in these two types of reaction indicate that the solvation of formaldehyde and/or hydrogen chloride molecules by nonpolar solvent molecules hardly exists, or that its effect is negligible.

This relatively large activation energy would similarly act as a barrier for the reaction to proceed fruitfully to yield BCME as the product. Furthermore, it is also obvious from the similar steepness of the Arrhenius

plot that, as the temperature decreases, the rate of the formation of BMCE decreases logarithmically and very fast. Therefore, the formation of BCME from formaldehyde and hydrogen chloride in the nonpolar condensed phase at ambient temperature will be similarly slow. The calculated rate constant for the nonpolar condensed phase ($C Cl_4$) reaction at 25° C is 0.1516 µl/µmole/min, one-fourth the value of the reaction at 40° C. Just a word of caution here: Do not compare this rate constant for the nonpolar condensed phase ($C Cl_4$) reaction (5-fold excess of HCl) with those for gas phase and polar condensed phase reactions. They are of different mechanisms and in different units.

TABLE 5

KINETIC MEASUREMENTS OF FORMATION OF BCME IN CARBON TETRACHLORIDE (9.8° C)

(HCHO/HCl = 0.00858 mole: 0.0429 mole = 1:5; solvent = 418 ml)

Time (hr.)	Sample Size (μℓ)	HCHO Peak Height/μℓ(Div.)	1/Peak Height/μℓ	Calibration
0.1	5	12.52	0.07987	1 μg = 28.73 Div.
0.25	5	13.40	0.07463	
1	5	12.96	0.07716	
1.25	5	13.28	0.07530	
20.0	5	10.32	0.09690	
20.5	5	9.76	0.10246	
20.75	5	10.00	0.10000	
49.0	5	6.96	0.14368	
49.1	5	6.96	0.14368	
76.6	5	6.12	0.16340	

Observed rate constant k = 2.027×10^{-2} μℓ/μmole/min.

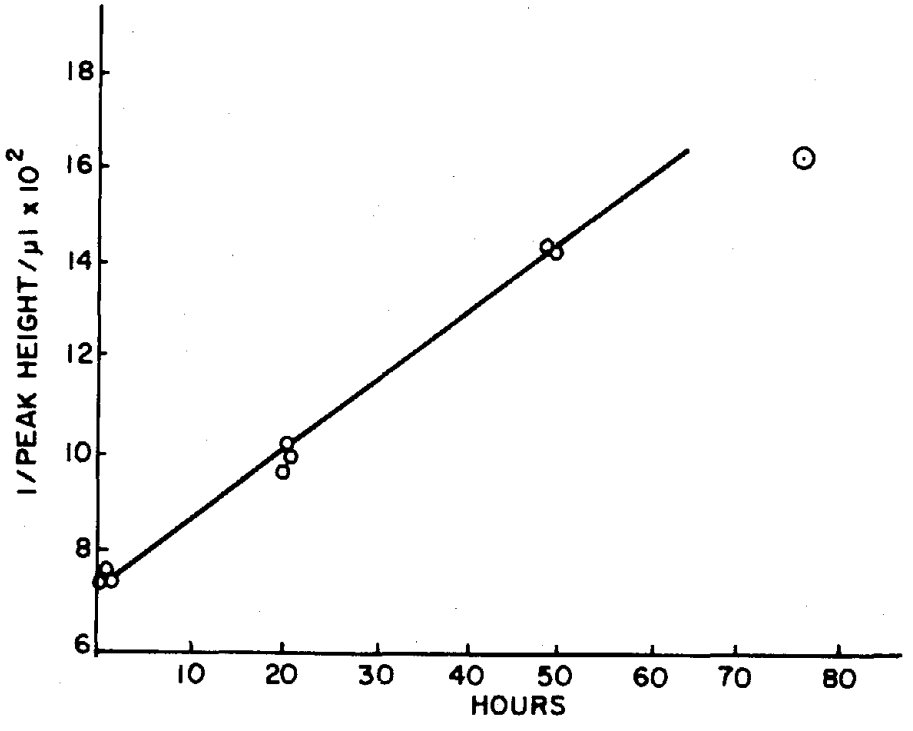


FIGURE 9. KINETIC PLOT FOR BCME FORMATION IN CARBON TETRACHLORIDE AT 9.8° C

TABLE 6

KINETIC MEASUREMENTS OF FORMATION OF BCME IN CARBON TETRACHLORIDE (19.7° C)

(HCHO/HCl = 0.007403 mole: 0.037071 mole = 1:5; solvent = 445 ml)

Time (min.)	Sample Size (μℓ)	HCHO Peak Height/μℓ(Div.)	1/Peak Height/μℓ	Calibration
3	5	26.8	0.03731	1 μg = 29.0 Div.
57	5	20.5	0.04878	
69	5	21.9	0.04566	
90	5	19.2	0.05208	
108	5	18.6	0.05376	

Observed rate constant k = 0.1358 μℓ/μmole/min.

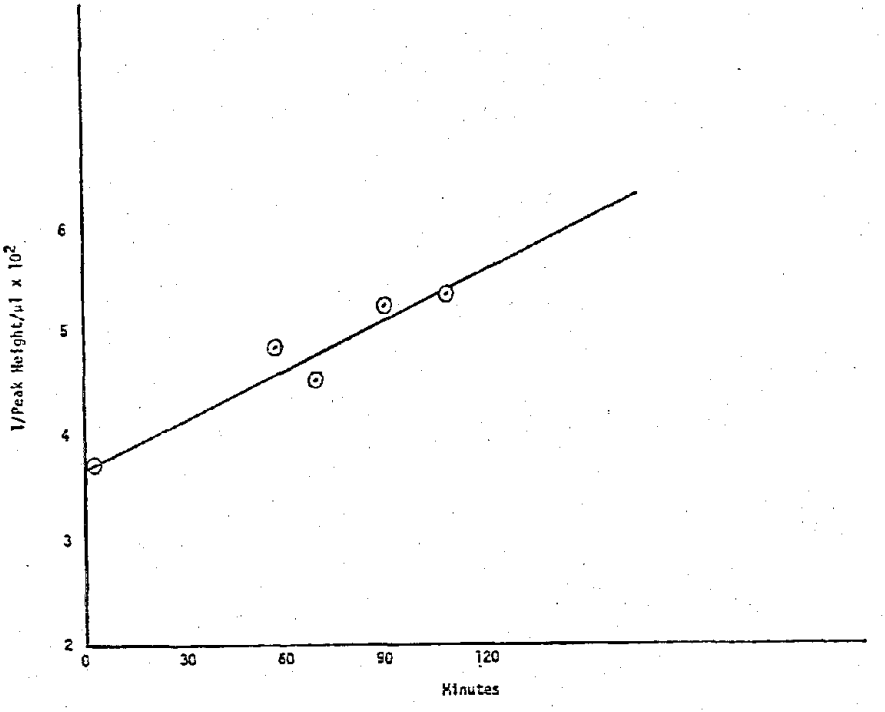


FIGURE 10. KINETIC PLOT FOR BCME FORMATION IN CARBON TETRACHLORIDE AT 19.7° C

TABLE 7

KINETIC MEASUREMENTS OF FORMATION OF BCME IN CARBON TETRACHLORIDE (40° C)

(HCHO/HCl = 0.009468 mole: 0.047297 mole = 1:5; solvent = 431 ml)

Time (min)	Sample Size (μℓ)	HCHO Peak Height/μℓ (Div.)	1/Peak Height/μℓ	Calibration
16	5	18.92	0.05285	1 μg = 28.62 Div.
30	5	15.08	0.06631	
45	5	13.68	0.07310	
90	5	12.96	0.07716	
19.5 hr.	5	12.72	0.07862	

Rate constant k = 0.5977 μℓ/μmole/min.

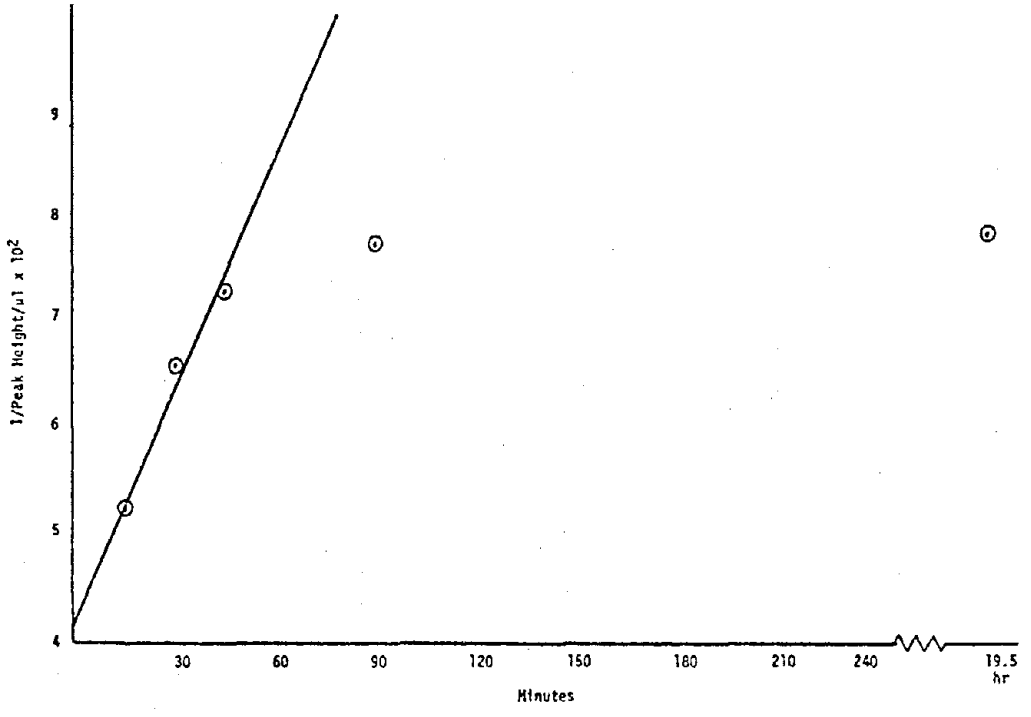


FIGURE 11. KINETIC PLOT FOR BCME FORMATION IN CARBON TETRACHLORIDE AT 40° C

TABLE 8

RATE CONSTANTS FOR BCME FORMATION IN CARBON TETRACHLORIDE

HCHO/HCl Ratio	Temperature (° C)	1/T	k(μℓ/μmole/min.)	log k
1/5	9.8	3.536×10^{-3}	2.027×10^{-2}	-1.6931
1/5	19.7	3.414×10^{-3}	0.1358	-0.8671
1/5	40.0	3.195×10^{-3}	0.5977	-0.2240

$E_{act.}$ = 18.9 Kcal/mole

$k_{25° C}$ (calculated) = 0.1518 μℓ/μmole/min.

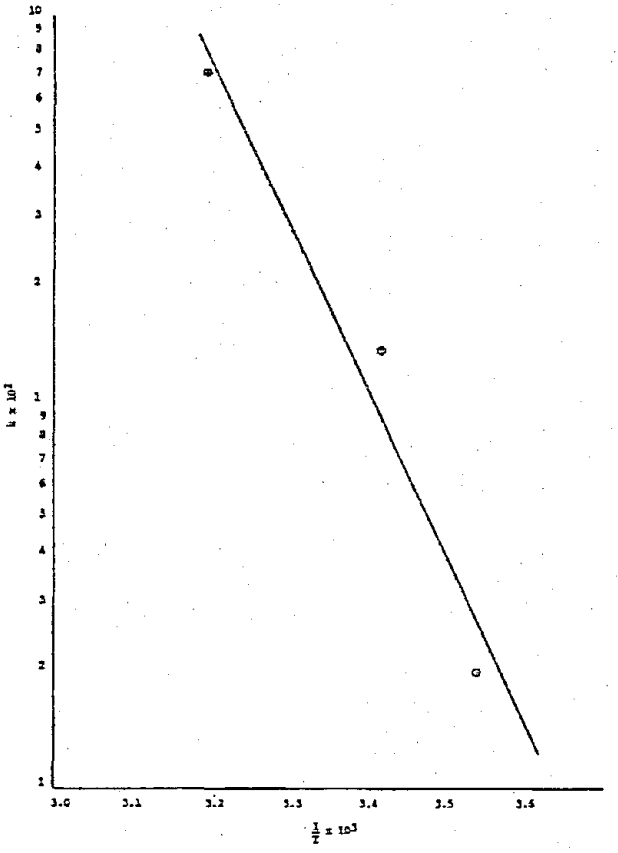


FIGURE 12. ARRHENIUS PLOT FOR BCME FORMATION IN CARBON TETRACHLORIDE

IX. BCME FORMATION IN THE POLAR CONDENSED PHASE

The apparatus for the kinetic study of BCME formation in methylene chloride is the same as that used in the study of the carbon tetrachloride system and is described in Section XVIII, Experimental.

The methylene chloride solutions of formaldehyde and of hydrogen chloride were prepared separately as in the case of the carbon tetrachloride system. The solubility of formaldehyde in methylene chloride is, as expected, greatly improved. These two solutions were cooled to the desired temperature and then mixed in the reactor, which was immersed in a constant-temperature bath. The method of mixing these solutions is, as in the case of carbon tetrachloride solutions, crucial to keeping the formaldehyde in solution. When formaldehyde solution was poured into hydrogen chloride solution with fast stirring, no polymerization of formaldehyde and precipitation of paraformaldehyde occurred . Reversed mode of addition, however, resulted in instant polymerization and precipitation. This phenomenon once more shows dramatically the dynamic equilibriums of formaldehyde, hydrogen chloride, and chloromethanol.

The reaction kinetics were similarly followed by the rate of disappearance of formaldehyde on account of its enhanced rate. The kinetic measurements and experimental conditions of each experiment in the methylene chloride systems are tabulated in Tables 9, 10, 11, 12, and 13. The corresponding plots are shown in Figures 13, 14, 15, 16, and 17. These experiments were conducted at a 1 to 1 ratio of formaldehyde to hydrogen chloride; the applicable integrated rate equation is therefore Eq. 4. The reaction is therefore of a second-order plot. The data and the graph for the Arrhenius plot are shown in Table 14 and Figure 18, respectively.

The slopes of all the graphs were determined by the least square treatment. All graphs were drawn by the linear regression method. All the rate constants were expressed in terms of milliliter, millimole, and minute by making use of the experimentally determined conversion factor. The activation energy for BCME formation in the polar condensed phase, calculated from the Arrhenius plot, is 5.24 Kcal per mole. The energy barrier in this case is much lower. The reaction can therefore proceed with ease, obviously by way of ionic mechanism. Furthermore, the greatly reduced slope of the Arrhenius plot indicates that the temperature effect on the reaction rate is relatively small. In other words, the reaction will proceed at only a slightly slower rate even at considerably lower temperature. The calculated rate constant for the polar condensed phase (CH_2Cl_2) reaction at 25° C is 0.1589 µl/µmole/min. Just a word of caution here: Do not compare this rate constant for the polar condensed phase (CH_2Cl_2) reaction with those for gas phase and nonpolar condensed phase reactions. They are of different mechanisms and in different units. Thus, regarding the possible formation of BCME in the industrial environment, attention should be focused on the polar condensed phase reaction.

To worsen the situation, unfortunately, the types of solvent systems used most often in industrial applications happen to be highly polar.

TABLE 9

KINETIC MEASUREMENTS OF FORMATION OF BCME IN METHYLENE CHLORIDE (0° C)

[HCHO/HCl = 1:1 (0.02363 mole each); solvent = 395.5 ml]

Time (min.)	Sample Size (μℓ)	HCHO Peak Height/μℓ	1/Peak Height/μℓ	Calibration
28	2	94.75	0.01055	1 μg = 28.83 Div.
127	2	74.0	0.01351	
193	2	59.5	0.01681	

Observed rate constant k = 0.06458 μℓ/μmole/min.

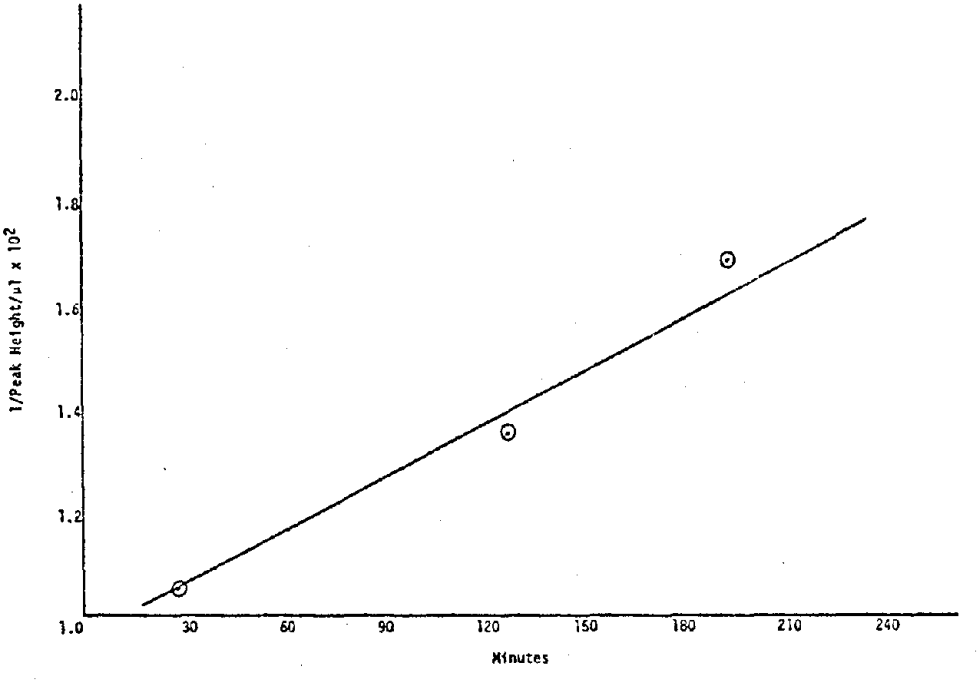


FIGURE 13. KINETIC PLOT FOR FORMATION OF BCME IN METHYLENE CHLORIDE AT 0° C
[HCHO/HCl = 1:1 (0.02363 mole); solvent = 395.5 ml]

TABLE 10

KINETIC MEASUREMENTS OF FORMATION OF BCME IN METHYLENE CHLORIDE (0° C)

[HCHO/HCl = 1:1 (0.02219 mole each); solvent = 484 ml]

Time (min.)	Sample Size (μℓ)	HCHO Peak Height/μℓ (Div.)	1/Peak Height/μℓ	Calibration
32	1	130.15	0.007683	1 μg = 31.03 Div.
90	1	94.26	0.010689	
169	1	73.99	0.013513	

Rate constant k = 0.07865 μℓ/μmole/min.

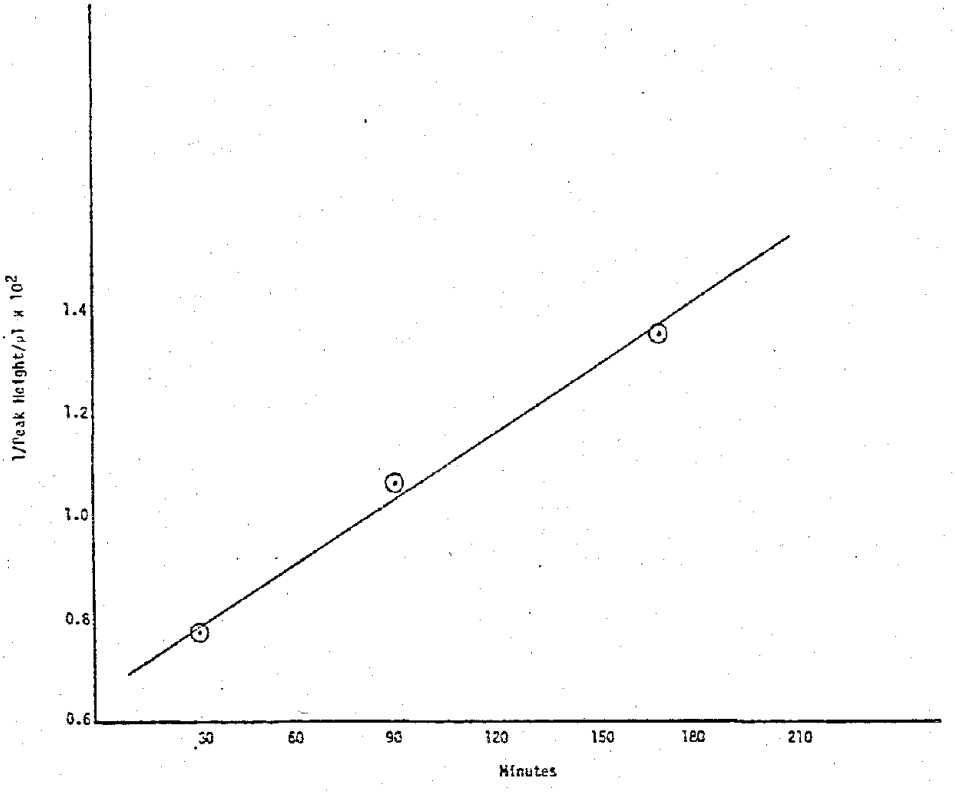


FIGURE 14. KINETIC PLOT FOR FORMATION OF BCME IN METHYLENE CHLORIDE AT 0° C
[HCHO/HCl = 1:1 (0.02219 mole); solvent = 484 ml]

TABLE 11

KINETIC MEASUREMENTS OF FORMATION OF BCME IN METHYLENE CHLORIDE (9.8° C)

[HCHO/HCl = 1:1 (0.031935 mole each); solvent = 368 ml]

Time (min.)	Sample Size (μℓ)	HCHO Peak Height/μℓ	1/Peak Height/μℓ	Calibration
5	2	37.6	0.02659	1 μg = 29 Div.
30	2	35.9	0.02786	
60	2	34.4	0.02907	
90	2	32.0	0.03125	
120	2	30.5	0.03278	
150	2	30.5	0.03278	
180	2	30.5	0.03278	

Rate constant k = 0.09475 μℓ/μmole/min.

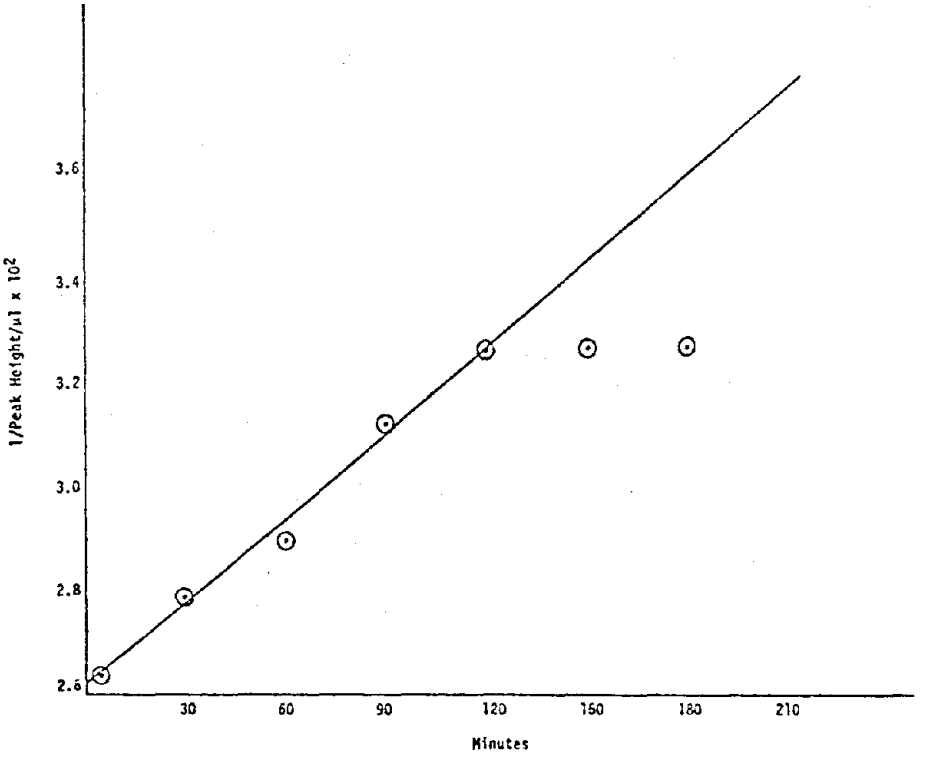


FIGURE 15. KINETIC PLOT FOR FORMATION OF BCME IN METHYLENE CHLORIDE AT 9.8° C [HCHO/HCl = 1:1 (0.031935 mole); solvent = 368 ml]

TABLE 12

KINETIC MEASUREMENTS OF FORMATION OF BCME IN METHYLENE CHLORIDE (9.8° C)

[HCHO/HCl = 1:1 (0.02628 mole each); solvent = 372 ml]

Time (min.)	Sample Size (µℓ)	HCHO Peak Height/µℓ	1/Peak Height/µℓ	Calibration
5	2	28.8	0.03472	1 µg = 29 Div.
30	2	27.4	0.03650	
60	2	26.7	0.03745	
180	2	22.3	0.04484	

Rate constant k = 0.9980 µℓ/µmole/min.

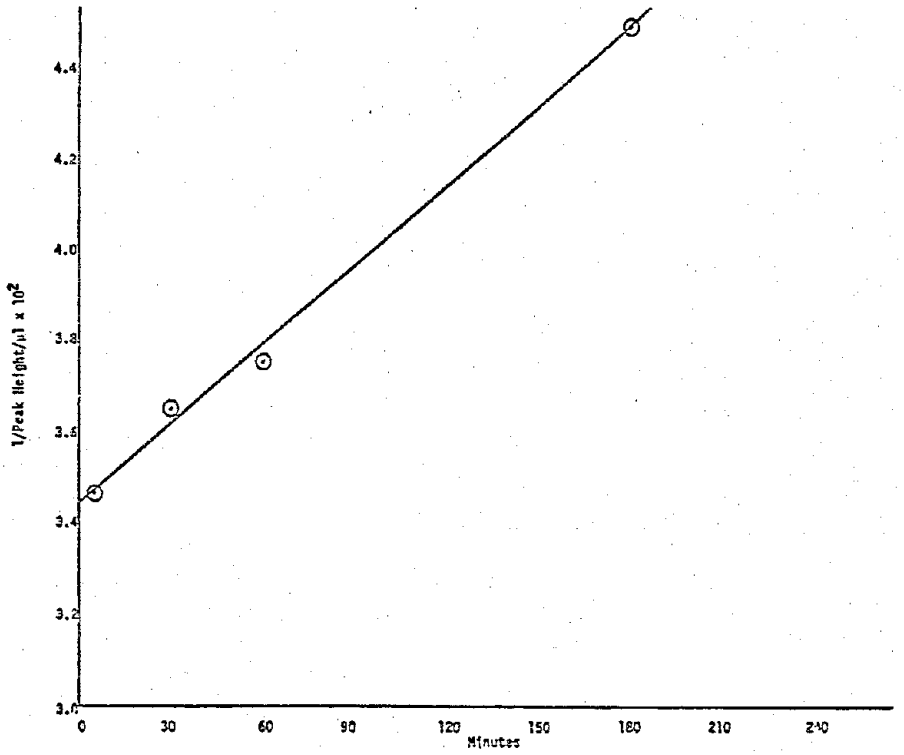


FIGURE 16. KINETIC PLOT FOR FORMATION OF BCME IN METHYLENE CHLORIDE AT 9.8° C [HCHO/HCl = 1:1 (0.02628 mole); solvent = 372 ml]

TABLE 13

KINETIC MEASUREMENTS OF FORMATION OF BCME IN METHYLENE CHLORIDE (19.7° C)

[HCHO/HCl = 1:1 (0.02995 mole each); solvent = 419 ml]

Time (min.)	Sample Size (µℓ)	HCHO Peak Height/µℓ	1/Peak Height/µℓ	Calibration
7	1	106.04	0.00943	1 µg = 31.98 Div.
14	1	98.95	0.01011	
26	1	95.11	0.01051	
40	1	83.78	0.01194	

Rate constant k = 0.1380 µℓ/µmole/min.

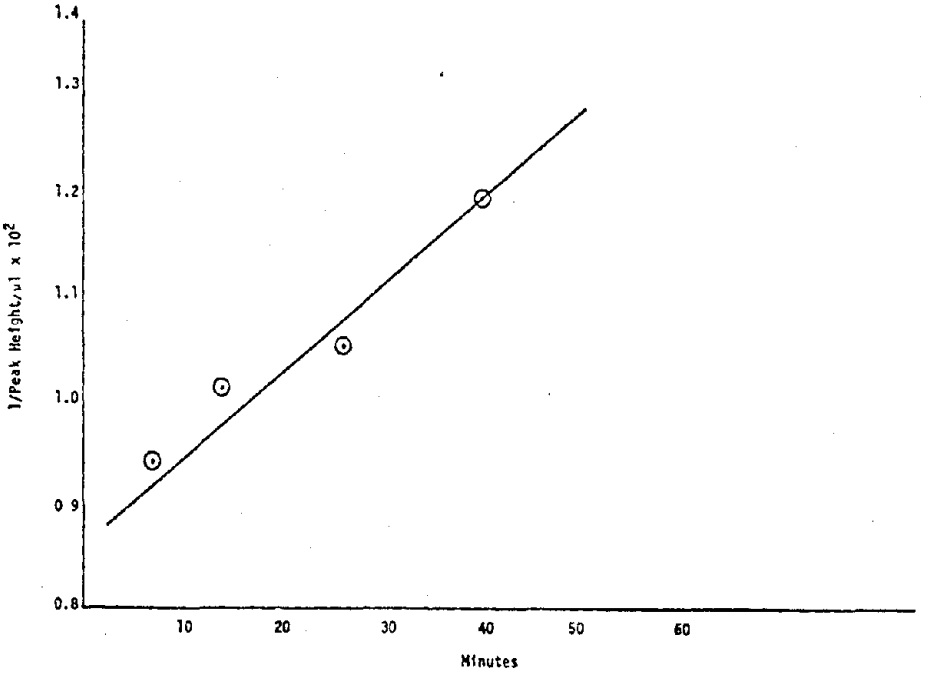


FIGURE 17. KINETIC PLOT OF FORMATION OF BCME IN METHYLENE CHLORIDE AT 19.7° C
[HCHO/HCl = 1:1 (0.02995 mole); solvent - 419 ml]

TABLE 14

RATE CONSTANTS FOR BCME FORMATION IN METHYLENE CHLORIDE

HCHO/HCl	Temperature (° C)	1/T	k(μℓ/μmole/min)	log k
1:1	0	3.663×10^{-3}	0.06458	-1.1899
1:1	0	3.663×10^{-3}	0.07865	-1.1043
1:1	9.8	3.536×10^{-3}	0.09475	-1.0234
1:1	9.8	3.536×10^{-3}	0.09980	-1.0009
1:1	19.7	3.416×10^{-3}	0.13800	-0.8602

E_{act} = 5.24 Kcal/mole

$k_{25° C}$ (calculated) = 0.1589 μℓ/μmole/min.

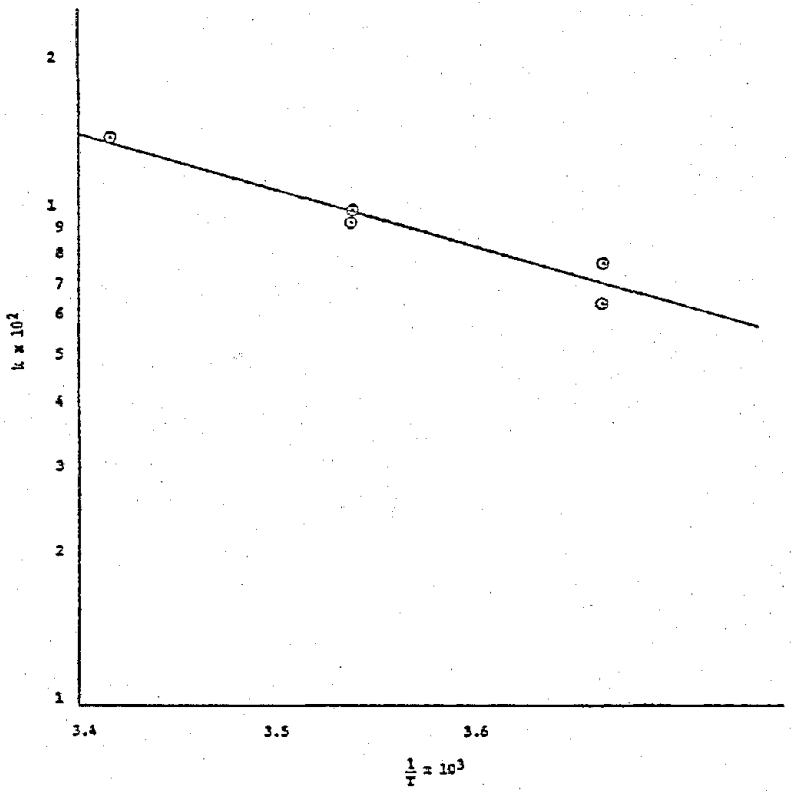


FIGURE 18. ARRHENIUS PLOT FOR BCME FORMATION IN METHYLENE CHLORIDE

X. ACTIVATION ENERGIES, ENTROPIES, AND SPONTANEITY OF BCME FORMATION

In all the natural processes, it is a truism that they will shift toward the direction that will result in less energy content and more molecular freedom for the products. For example, water will flow toward the lower ground so that it can lower its potential energy. A jigsaw puzzle will tend to become scattered in pieces and will never automatically return to its orderly arrangement of the whole.

In the formation of BCME in the gas phase, relatively large molecules are produced from four small molecules (two formaldehyde and two hydrogen chlorides). There is evidently a decrease in the freedom of the molecules involved in the process of transformation from the reactants to the products. In other words, there is a decrease in entropy. Furthermore, the activation energy is 19.8 Kcal/mole. Therefore, the BCME formation will not likely take place spontaneously under ambient conditions.

In the formations of BCME in the nonpolar condensed phase (carbon tetrachloride), the activation energy is 18.9 Kcal/mole, being essentially in the same magnitude as that for gas phase reaction. Apparently, no extensive solvation was involved to reduce the energy barrier. Furthermore, the molecules of formaldehyde, hydrogen chloride, and BCME behave individually in essentially the same way as in the gas phase and, therefore, there is no drastic change in their relative entropies. Thus, the BCME formation in the nonpolar condensed phase is again likely to be very slow under ambient conditions.

In the formation of BCME in the polar condensed phase (methylene chloride), the activation energy is about 5.24 Kcal/mole, indicating that BCME can be formed in polar media with facility by way of ionic-type mechanism. Obviously, solvation plays an important role in lowering its energy barrier.

XI. DECOMPOSITION OF BCME

While BCME is formed from formaldehyde and hydrogen chloride in the gas phase, it also undergoes thermal decomposition. By keeping 4,670 ppm formaldehyde and 4,670 ppm hydrogen chloride at 86° C for 28.3 hours, 0.65 ppm BCME was obtained (0.014 mole percent yield). On the other hand, 5.8 µl BCME kept under vacuum at 91° C for 18.3 hours gave 12.94 percent formaldehyde.

Furthermore, BCME also undergoes acid decomposition. The following data were obtained during the testing of the chromotropic acid method of determination of formaldehyde content. BCME (10 µl in 100 µl carbon disulfide) was added to 4 ml of water, followed by 0.1 ml of 1 percent chromotropic acid and 6 ml of concentrated sulfuric acid. The solution became very hot (about 80° C) at this time. After cooling, the formaldehyde content in the sample was read from the absorbance at 580 mµ from Spectro-20, indicating a 50.84 percent decomposition of BCME occurred. Similarly, 100 µg BCME in 8 µl hexane was treated the same way; a 20.53 percent decomposition was noted. The difference is possibly due to the fast evaporation of carbon disulfide, and therefore some BCME was lost, owing to entrainment. BCME also undergoes base-catalyzed decomposition. As a matter of fact, this is the usual way to destroy BCME in laboratory spillage.

XII. FORMATION OF BCME IN AQUEOUS MEDIUM

In spite of the extensive thermal and chemical decompositions described in Section XI, BCME has been, since 1887, routinely prepared from paraformaldehyde and chlorides in aqueous medium and isolated in the pure state up to 81 percent yield by fractionation from the crude product. [7,8] The presence of BCME was further identified in aqueous solution of formaldehyde and chlorides by NMR. [10] Based on the difference of activation energies of BCME formation in carbon tetrachloride (18.9 Kcal/mole) and in methylene chloride (5.24 Kcal/mole), its formation in aqueous phase would be expected to proceed with ease. The extent of its subsequent hydrolysis is entirely another matter, depending on its concentration, the temperature, and residence time. Thus, experiments were conducted of aqueous solution of formaldehyde with hydrochloric acid as well as magnesium chloride. To avoid or minimize the subsequent hydrolysis of BCME, the aqueous reaction mixtures were covered with organic layers so that the BCME would be instantly extracted to the organic layer as soon as it was formed. It is worth noting that the BCME yields varied inversely with reaction temperatures, indicating, apparently, that greater decomposition occurred at higher temperatures.

Furthermore, on addition of chlorosulfonic acid, the BCME yield increased 23-fold even at 10° C, strongly indicating the ionic nature of the reaction mechanism and supporting the cited high yield of BCME in the aqueous system. [7,8] All these data are tabulated in Table 15, and the dramatic increase of BCME yield is shown in Figure 19. Furthermore, it is clear from the plot that the BCME formation proceeded rather fast and reached a low plateau at a very early stage. The BCME yield, however, increased steeply on addition of chlorosulfonic acid, followed by a period of rapid acid decomposition. (For monitoring BCME, see Section XVIII, Experimental.)

TABLE 15

BCME FORMATION IN AQUEOUS-ORGANIC DOUBLE LAYERS

Water	Covering Solvent	Formaldehyde and Chlorides (mole)	Reaction Temp. (°C)	BCME Yields (mole%)	Yields After Addition of 20 ml Chlorosulfonic Acid (mole%)
300	Hexane (100 ml)	HCHO/HCl (0.1/0.1)	0	0.007	--
300	Hexane (100 ml)	HCHO/$MgCl_2$ (0.1/0.1)	0	0.027	--
300	Toluene (100 ml)	HCHO/HCl (0.46/0.46)	10	0.0024	0.0552
300	Benzene	HCHO/HCl (0.1/0.1)	30	0	--

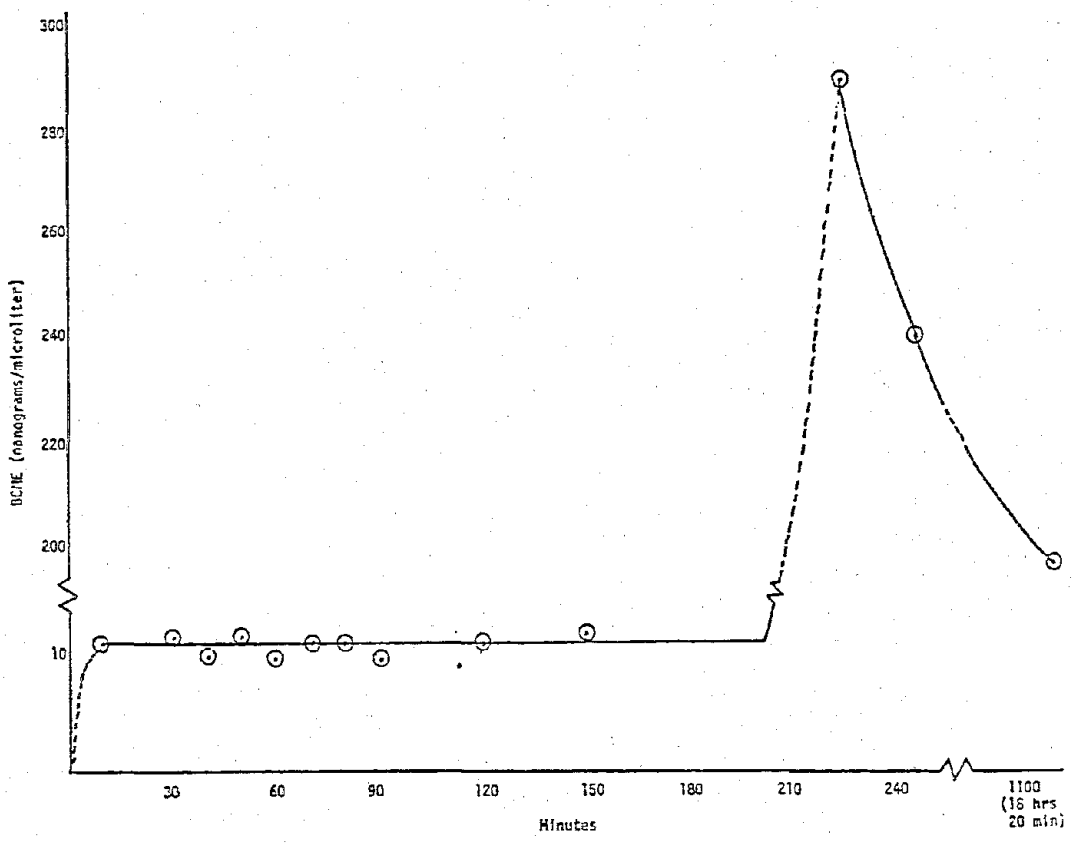


FIGURE 19. EFFECT OF CHLOROSULFONIC ACID ON BCME FORMATION IN AQUEOUS PHASE

XIII. THE MEDIUM IN WHICH BCME IS FORMED

Since there were aqueous as well as organic layers in the preceding experiments, the BCME could conceivably be first formed in the aqueous layer and subsequently migrated into the organic layer; or, formaldehyde and chlorides could diffuse into the organic layer first, and BMCE be formed there afterwards. An attempt was made to identify the medium (aqueous or organic) in which BCME was formed by observing the kinetic order of the reaction. For, in the latter case, the reaction is expected to be diffusion-controlled, the reacted reactants in the organic layer will be instantaneously replenished from the aqueous phase, and its rate equation should be of zero order as it is shown in the following derivation:

$$\frac{d[BCME]}{dt} = k[HCHO]^x[HCl]^y$$

$$= k[HCHO]^0[HCl]^0$$

$$= k$$

$$d[BCME] = kdt$$

$$\int_0^t d[BCME] = k\int_0^t dt$$

$$[BCME]_t = -kt + [BCME]_0$$

$$[BCME]_t = kt$$

A non-zero order plot would indicate that the reaction took place in the aqueous layer. The kinetic measurements and experimental conditions of this experiment in aqueous-organic double layer system are tabulated in Table 16. The corresponding plot is shown in Figure 20.

This experiment was conducted at a 1 to 1 ratio of formaldehyde to hydrochloric acid; the applicable integrated rate equation is therefore Eq. 4.

The linear plot of Figure 20 established a second-order kinetics, in other words, a non-zero order. Thus, the formation of BCME had to occur in the aqueous layer.

TABLE 16

KINETIC MEASUREMENTS OF BCME IN AQUEOUS-ORGANIC DOUBLE LAYER (0° C)

[HCHO/HCl = 1:1 (0.1085 mole each); water = 310 ml, Pentane = 100 ml]

Time (min.)	Aqueous Sample Size (µl)	HCHO Peak Height/µl	1/Peak Height/µl
0	1	1272	7.8616×10^{-4}
15	1	1180	8.4746×10^{-4}
30	1	1060	9.4340×10^{-4}
45	1	1078	9.2764×10^{-4}
75	1	970	10.3093×10^{-4}

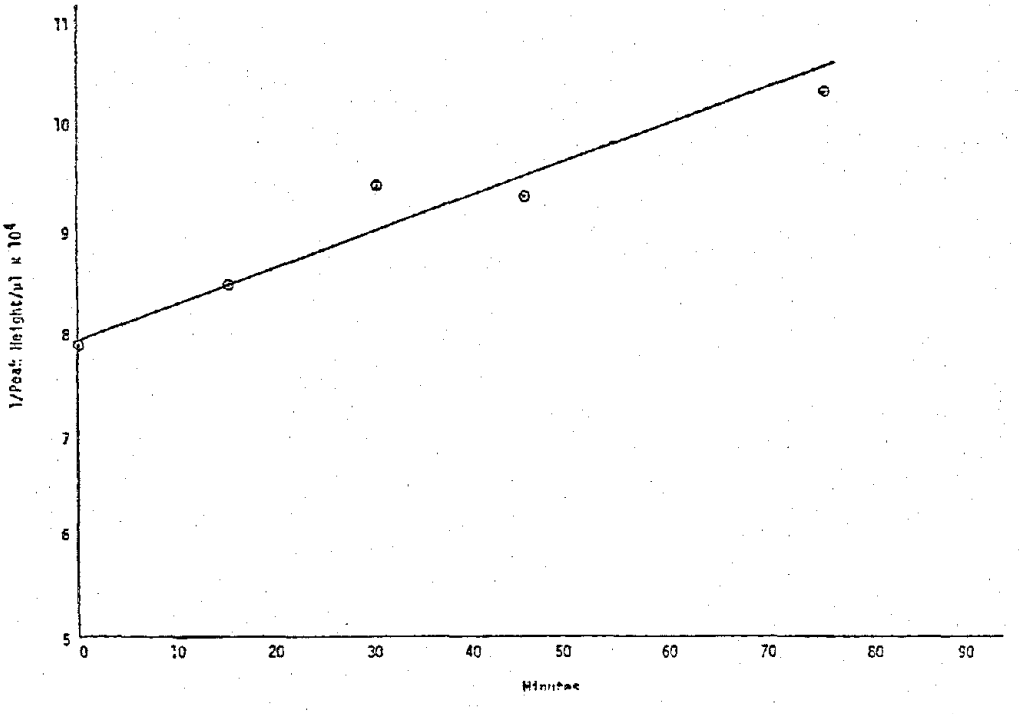


FIGURE 20. KINETIC MEASUREMENTS OF BCME FORMATION IN AQUEOUS-ORGANIC DOUBLE LAYERS (0° C)

XIV. REACTION ORDER AND MECHANISM OF BCME FORMATION

For the gas phase reactions with equivalent amounts of formaldehyde and hydrogen chloride, the data fit a third-order kinetic plot. The reaction apparently proceeds through chloromethanol intermediate. The formation and subsequent collapse of the 4-centered transition state of two chloromethanol molecules give BCME as the final product (see Figure 1, Path A).

$$HCHO + HCl \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ClCH_2OH$$

$$2ClCH_2OH \xrightarrow{k_2} ClCH_2OCH_2Cl + H_2O$$

The second equation is the rate-controlling step.

$$\frac{d[BCME]}{dt} = -\frac{d[ClCH_2OH]}{2dt} = k_2[ClCH_2OH]^2$$

But $[ClCH_2OH] = K_e[HCHO]\,[HCl]$

$$-\frac{K_e}{2}\frac{d[HCHO]\,[HCl]}{dt} = k_2K_e^{\,2}\,[HCHO]^2[HCl]^2$$

$$-\frac{d[HCHO]\,[HCl]}{dt} = 2k_2K_e\,[HCHO]^2[HCl]^2$$

When HCHO and HCl are at equivalent concentrations,

$$-\frac{dx^2}{dt} = 2k_2K_ex^4$$

$$-2x\frac{dx}{dt} = 2k_2K_ex^4$$

$$-\frac{dx}{dt} = k_{obs}x^3$$

$$-\int \frac{dx}{x^3} = k_{obs} \int dt$$

$$\frac{1}{x^2} = k_{obs} t + \frac{1}{x_o^2} \qquad \text{(Eq. 6)}$$

This is, therefore, the applicable integrated equation. With regard to the stability of the reacting mixture, it is essential that there must be enough (equivalent amount at least) hydrogen chloride present to prevent the spontaneous polymerization of formaldehyde.

For the nonpolar condensed phase reactions with large excess (5-fold) of hydrogen chloride, the data fit a pseudo second-order kinetic plot.

The reaction apparently proceeds through chloromethanol intermediate which adds slowly to the carbonyl function of a formaldehyde to give the chloromethoxymethanol. A bimolecular displacement yields the BCME as the final product (see Figure 2, Path A).

$$HCHO + HCl \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ClCH_2OH$$

$$ClCH_2OH + HCHO \xrightarrow[\text{slow}]{k_2} ClCH_2OCH_2OH$$

$$ClCH_2OCH_2OH + HCl \xrightarrow[\text{fast}]{k_3} ClCH_2OCH_2Cl + H_2O$$

The second equation is the rate-controlling step.

$$\frac{d[BCME]}{dt} = k_3[ClCH_2OCH_2OH]\,[HCl]$$

$$= \frac{d[ClCH_2OCH_2OH]}{dt}$$

$$= -\frac{d[ClCH_2OH]}{dt} = k_2[ClCH_2OH]\,[HCHO]$$

But $[ClCH\ OH] = K_e[HCHO]\ [HCl]$

$$-\frac{d[ClCH_2OH]}{dt} = -K_e\frac{d[HCHO]\ [HCl]}{dt} = k_2K_e[HCHO]^2[HCl]$$

But HCl is in large excess,

$$-\frac{d[HCHO]}{dt} = k_{obs}[HCHO]^2$$

$$-\frac{dx}{dt} = k_{obs}x^2$$

$$-\int\frac{dx}{x^2} = k_{obs}\int dt$$

$$\frac{1}{x} = k_{obs}t + \frac{1}{x_o} \qquad \text{(Eq. 7)}$$

This is, therefore, the applicable integrated rate equation.

For the nonpolar condensed phase reaction, the experiments were of necessity carried out at lower temperatures to maintain liquid state. Five-fold excess of hydrogen chloride was used to speed up the reaction for the sake of convenience. At the same time, the excess hydrogen chloride insured the stability of the reacting mixture from the spontaneous polymerization of formaldehyde.

For the polar condensed phase reactions with equivalent amounts of formaldehyde and hydrogen chloride, the data fit a second-order kinetic plot. The reaction apparently proceeds through chloromethanol intermediate which adds to the carbonyl function of formaldehyde to form the chloromethoxymethanol. The latter (which dissociates more favorably than does chloromethanol on resonance ground) dissociates, as all unimolecular substitution, predominately to give chloromethyoxymethyl carbonium ion and ultimately yields BCME as the final product (see Figure 3, Path A).

$$HCHO + HCl \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ClCH_2OH$$

$$ClCH_2OH + HCHO \xrightarrow{k_2} ClCH_2OCH_2OH$$

$$ClCH_2OCH_2OH \xrightarrow{k_3} ClCH_2OCH_2^+ + OH^-$$

$$ClCH_2OCH_2^+ + Cl^- \xrightarrow{k_4} ClCH_2OCH_2Cl$$

The second equation is the rate-controlling step.

$$\frac{d[BCME]}{dt} = -\frac{d[ClCH_2OCH_2^+]}{dt} = \frac{d[ClCH_2OCH_2OH]}{dt}$$

$$= -\frac{d[ClCH_2OH]}{dt} = k_2[ClCH_2OH]\,[HCHO]$$

But $[ClCH_2OH] = K_e[HCHO]\,[HCl]$

$$-K_e\frac{d[HCHO]\,[HCl]}{dt} = K_e k_2[HCHO]^2[HCl]$$

When HCHO and HCl are at equivalent concentrations,

$$-\frac{dx^2}{dt} = k_2x^3$$

$$-2x\frac{dx}{dt} = k_2x^3$$

$$-\frac{dx}{dt} = k_{obs}x^2$$

$$-\int\frac{dx}{x^2} = k_{obs}\int dt$$

$$\frac{1}{x} = k_{obs}t + \frac{1}{x_o} \qquad \text{(Eq. 8)}$$

This is, therefore, the applicable integrated rate equation.

With regard to the stability of the reacting mixture, it is essential that there must be enough (equivalent amount at least) hydrogen chloride present to prevent the spontaneous polymerization of formaldehyde.

XV. EFFECT OF MOISTURE ON THE FORMATION OF BCME

It was reported that the yield of BCME in gas phase was consistently lower in a dry atmosphere but not significantly diffierent under various ambient humidities [13]. It is, therefore, clear that the water molecules do participate in the formation of BCME. The cited experiments were carried out at 100 ppm levels, and the moisture content in the atmosphere of a 50 percent relative humidity was about 150 times in excess. Furthermore, since the activation energy in the dry gas phase is 19.8 Kcal/mole, and that in the polar condensed phase is 5.24 Kcal/mole, the BCME formation, even in the gas phase, may very well take place in water clusters or droplets. This unsuspected presence of relative abundance of water molecules naturally would mask its effect on the reaction.

Furthermore, these clusters or droplets of polar solvents can be either airborne or adsorbed surface film on stationary objects or on airborne particulates. Thus, the locality of reaction is actually in the polar condensed phase regardless of whether it is in the air, in the surface film, or in the main body of reaction mixture. Only in these media is the rate of BCME formation greatly enhanced. One should not lose sight of this aspect, particularly from the viewpoint of industrial hygiene.

XVI. EVALUATION OF BCME TRAPPING TECHNIQUES FOR THE FIELD SURVEY

Details of the experimental techniques of following the kinetics of BCME formation in gas phase and condensed phases are described in Section XVIII, Experimental. The comparative evaluation of the sample trapping methods and the final adoption of the selected ones for use in the on-site survey are discussed here.

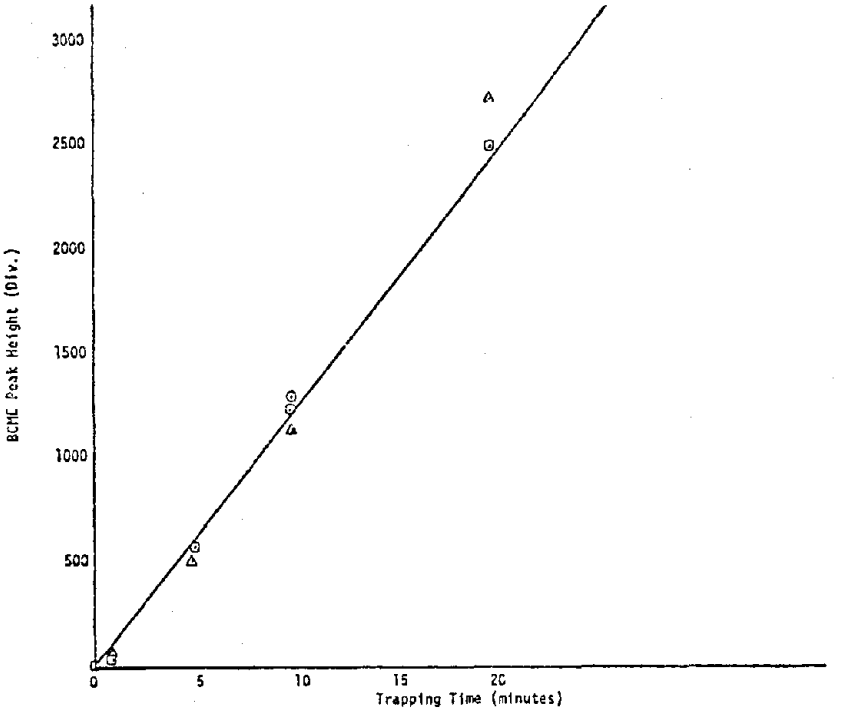
For the collection of air samples during the on-site survey for the detection of BCME from breathing zones and from area monitoring, samples were retained either by adsorption on packing materials in stainless steel, 1-inch by 1/4-inch trapping tubes, or by transformation to its stable derivatives in gas samplers containing more than enough derivatization reagents to react with the anticipated incoming BCME.

For the evaluation of trapping techniques in the laboratory, the BCME source was the two permeation tubes of 10 inches in length, furnished and certified by Metronics, which release at 30° C 130±5% and 140±5% ng/min., respectively. The release rate of BCME by a permeation tube is dependent on the temperature and the length of the tube. A fast flow of carrier gas gives a dilute stream and a slow flow of carrier gas gives a more concentrated stream. The total amount of BCME is dependent on trapping time only. In the evaluation test, the flowrate was set at 400 ml/min. The trapping times were accurately measured by a timer.

A. Performance and Efficiency of Sample Trapping Materials by Adsorption

Several polymer beads were commercially available and could potentially be used for sample trapping purposes, such as Porapak Q, Chromosorb 101, and Tenax G.C. All materials were preconditioned in a U-tube at 200 - 225° C overnight with either nitrogen or helium constantly flowing through before use. The performances

of these materials were tested by first passing a stream of known amount (140 ng/min) of BCME from a permeation tube at 30° C and constant carrier gas flowrate of 400 ml/min. through trapping tubes for 1, 5, 10, and 20 minutes, and then thermally flashing the retained BCME on the absorbents by a Bendix Flasher onto a gas chromatograph analytical column. The peak heights of G.C. responses were plotted against trapping times (Figure 21). It is evident that Porapak Q, Chromosorb 101, and Tenax G.C. all not only performed satisfactorily, but also checked remarkably with one another. The proximities of dots of same trapping times indicate the precision, and the linearity of the plot depicts the accuracy.



Trapping Tube: △ = Porapak Q, ⊙ = Chromosorb 101, ⊡ = Tenax G.C.
Column: 1.5' x 3/16" Copper 0.4% Carbowax 1500 on Carbopack A
Temperature Program: 30-120° C @ 32°/min.
Detector: FID @ 250°
Carrier: He 25 ml/min.

FIGURE 21. COMPARATIVE EVALUATION OF THE EFFICIENCY OF TRAPPING MATERIALS

Similarly, the efficiencies of the trapping materials were tested by placing two trapping tubes of the same packing materials in series in the stream of a BCME permeation tube. The backup tubes were flashed and analyzed by G.C. every 30 minutes. No detectable BCME breakthrough was found after 2 hours collection on Porapak Q, Chromosorb 101 or, Tenax G.C.

Based on these results, any one of these tested materials could be used, but Porapak Q was selected for air-sample trapping purposes solely because of its lowest cost.

B. Sample Trapping by Derivatization

Air samples were, by means of a monitoring pump, bubbled through a derivatization solution inside a bubbler where BCME was transformed to a stable derivative. The performance and efficiency of this approach will be discussed in Section XVII in conjunction with the evaluation of analytical procedures.

XVII. EVALUATION OF BCME ANALYTICAL TECHNIQUES FOR THE FIELD SURVEY

There are conceivably six methods for analysis of BCME:

A. Direct Gas Chromatography (G.C.)

B. On-Column Concentration - G.C.

C. Adsorber-G.C. (single or dual columns)

D. Derivatization - G.C.

E. Adsorber - Mass Spectrometry (M.S.)

F. Adsorber - G.C.-M.S.

For their experimental details, see cited references and Section XVIII.

A. Direct Gas Chromatography (G.C.)

The direct gas chromatography is not applicable, owing to its incapability for the detection in ppb level of BCME in the actual workplace.

B. On-Column Concentration - G.C. Method

The on-column concentration - G.C. method [16], using a column of Porapak Q and S as packing materials and a microcoulometer detector, effects on-column concentration without resorting to solvent-scrubbing or cryogenic trap, eliminates superfluous peaks, and conducts the analysis on the same column. However, this technique is applicable for stationary monitoring but not convenient for mobile field survey.

C. Adsorber - G.C. Method

The adsorber - G.C. method comprises two stages. The first stage is to trap the pollutants by adsorption on the packing materials in a trapping tube as discussed in the preceding section. The second stage is to thermally flash the adsorbates onto a G.C. analytic

column. An extensive study on a combination of Chromosorb 101 trapping tube and a Chromosorb 101 analytical G.C. column was reported. [17] The trapped BCME could be kept for 2 weeks without deterioration.

In the evaluation of the G.C. analytical columns, two were under consideration. One is the Chromosorb 101 column, and its use has been reported. [17] The other is 0.4 percent Carbowax 1500 on Carbopak A column. Various amounts of BCME from a permeation tube at constant temperature (30° C) and flowrate (400 ml/min) were first trapped on trapping tubes. The amounts, as explained in Section XVI, are directly proportional to the trapping times. These various amounts of trapped BCME were then thermally flashed onto the analytical column in question and its corresponding peak height responses recorded. The linearity of the plot of G.C. peak height responses versus trapping time is taken as the criterion of satisfactory performance for the column. The plot of the Chromosorb 101 column and that of the 0.4 Carbowax 1500 on Carbopack A column are shown in Figures 22 and 23, respectively. Their detectable limits (defined as twice the noise height) and sensitivity factors are listed in Table 17.

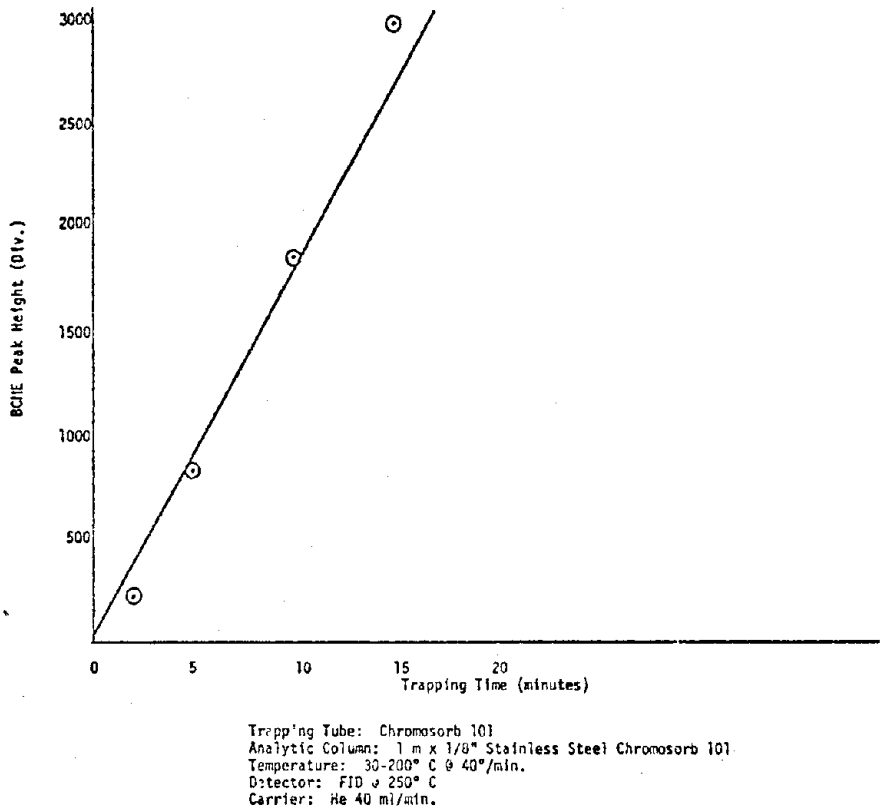


FIGURE 22. LINEARITY OF CHROMOSORB 101 ANALYTICAL COLUMN PERFORMANCE

Obviously, both columns performed well. With the Chromosorb 101 column, the low adsorption organics in the air all escaped by desorption in the early stage during the transfer by thermal flashing of the adsorbates onto the column at ambient temperature. With the Carbowax-on-Carbopack column, some of these organics were resolved during the early isothermal stage, and other contaminants, including BCME, formed a good chromatogram in the temperature programmed stage. Therefore, it is possible to identify some of these organics if one wants to.

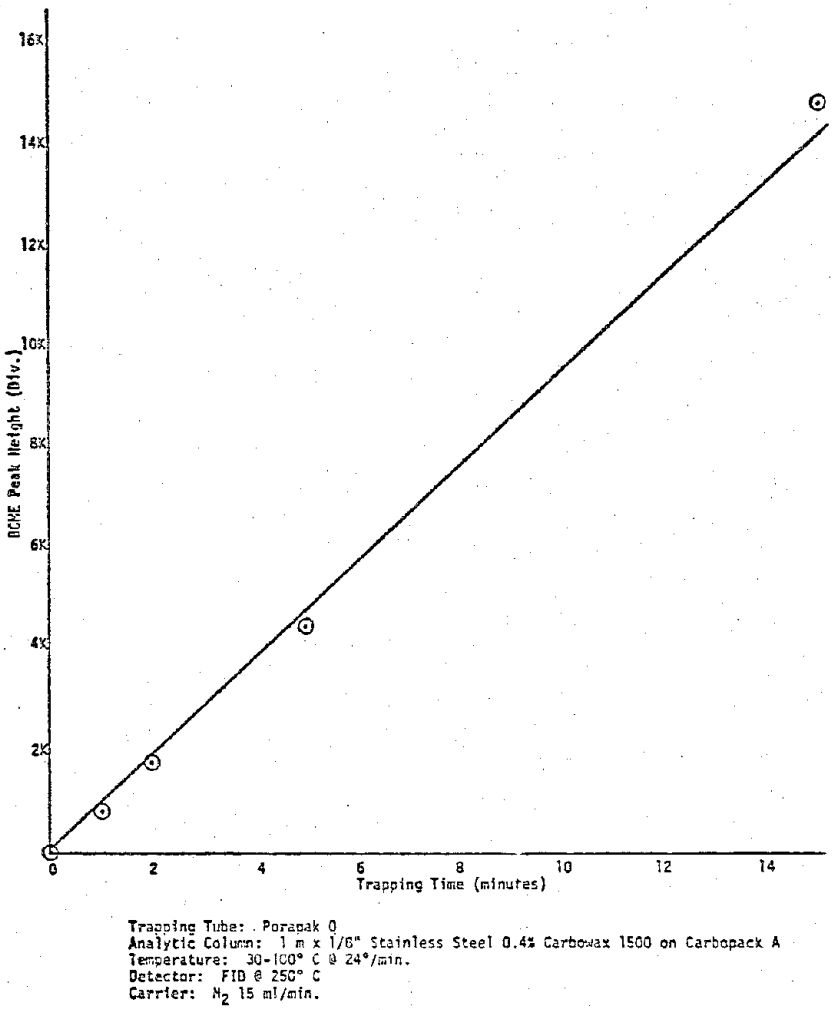


FIGURE 23. LINEARITY OF CARBOWAX-ON-CARBOPACK ANALYTICAL COLUMN PERFORMANCE

TABLE 17

EVALUATION OF ANALYTICAL COLUMNS

Method	Trapping Tube	Analytical Column	Detectable Limit (ng)	Sensitivity Factor (ng/div)
Trapping Sampler and G.C.	Porapak Q 3" x 1/4" 250 mg	0.4% Carbowax-on-Carbopack A 1 m x 1/8" s.s.	1.2	0.12
Trapping Sampler and G.C.	Chromosorb 101 3" x 1/4" 200 mg	Chromosorb 101 100/120 mesh	4.7	0.47

Furthermore, because of the ease with which Chromosorb 101 became contaminated by pollutants in the air, the Carbowax-on-Carbopack column was chosen on occasions for analysis of BCME in the laboratory when it was certain there were no interferences present in the samples.

A gas chromatographic system [18] employing a primary adsorber and two analytical columns gated in sequence was also reported and patented. This system is capable in determining in ppb level BCME as well as other materials in a background of ppm level of various other components. It is useful for stationary central monitoring of several suspected areas of a plant, but not suitable for mobile personnel monitoring.

D. Derivatization - G.C. Method

The derivatization - G.C. method was developed by Dow Chemical Company chemists. [19] The BCME was first converted into a derivative of trichlorophenol in methanol, which, in turn, was analyzed on a column, with its packing materials prepared by Dow chemists. This column is claimed by Dow Chemical as proprietary. With the Contracting Officer's approval, a secrecy agreement was signed between Dow Chemical and Bendix, Special Projects, allowing Bendix to use this column in connection with this project only and in no way to reveal it. The derivative was identified as $Cl_3C_6H_2OCH_2OCH_2OCH_3$.

This method seemed to have the obvious advantage of eliminating potential interfering matters which might exist in the industrial

environment and thus might cover up the chromatogram peak in question. Decision was therefore made to evaluate it in more detail.

The cited preparation of the derivative reagent was to use 25 grams sodium methoxide and 5 grams 2,4,6-trichlorophenol in 1 liter of methanol. This constituted an 18-fold excess of sodium methoxide. The recoveries varied from 86 to 115 percent (Table II in the cited paper [19]).

It was rather puzzling that an 18-fold excess of sodium methoxide was employed in spite of the known fact that sodium methoxide had a destructive effect on BCME besides furnishing the trichlorophenolate. Plots were therefore made of the data in Table III of the cited paper, [19] using both the G.C.-M.S. responses and the derivative-G.C. responses versus corresponding BCME added, as shown in Figures 24 and 25. Both plots are somewhat scattered, but the relative magnitudes of the statistically determined slopes (0.94 for Figure 24, 0.89 for Figure 25) indicate, in the latter case, the presence of the adverse effect of the excess sodium methoxide. Nevertheless, the close similarity of these two plots seemed to indicate that the derivative-G.C. method could be adopted as a convenient means of monitoring BCME.

It was interesting at the very end of the cited paper [19], that a statement was made to the effect that the sensitivity could be increased 6- or 8-fold by using stoichiometric quantities of sodium methoxide and 2,4,6-trichlorophenol, with recoveries varying from 82 to 100 percent (Table V in the cited paper [19]). Plot (Figure 26)

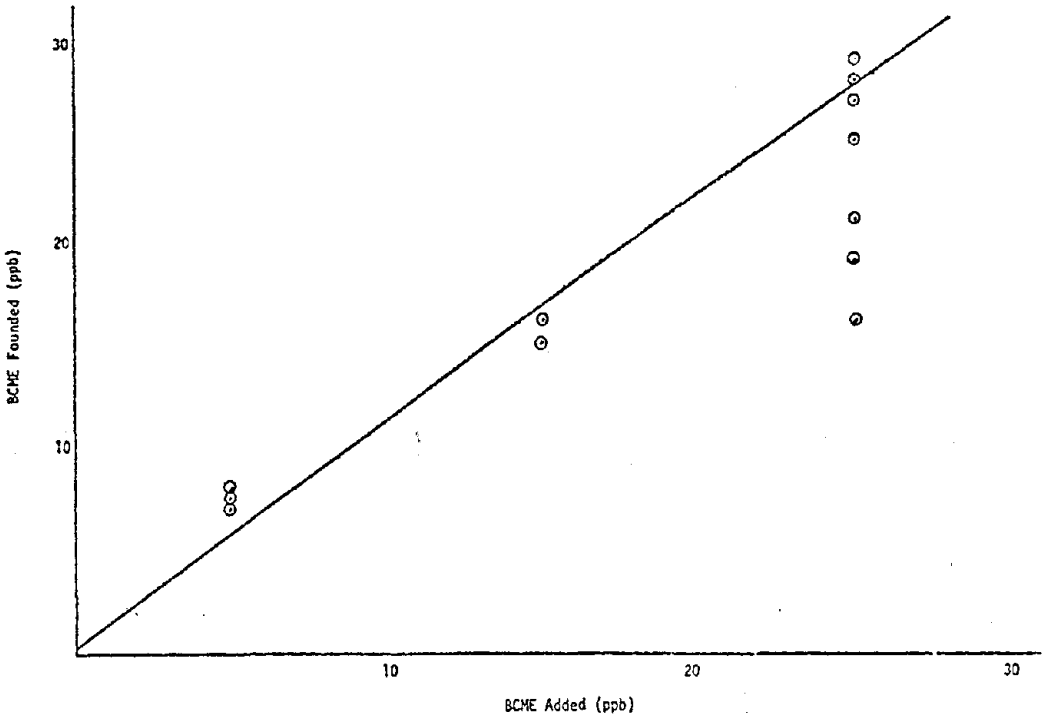


FIGURE 24. ANALYSES OF AIR FOR DETERMINATION OF BCME USING THE G.C. DERIVATIVE AND THE G.C.-M.S. TECHNIQUES (G.C.-M.S.)

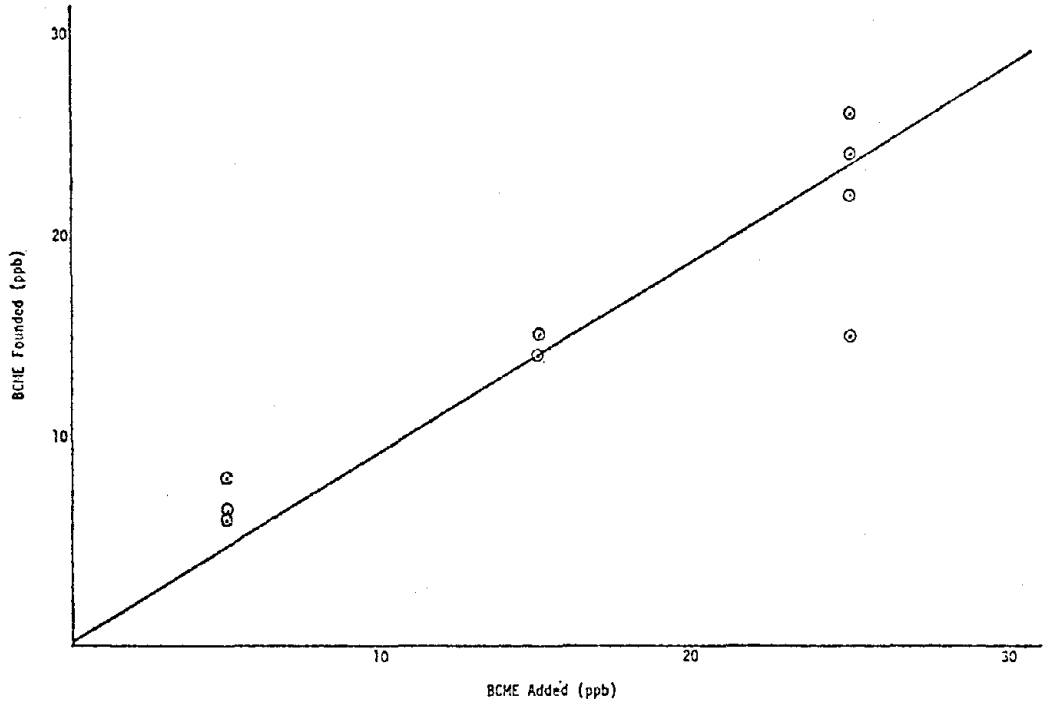


FIGURE 25. ANALYSES OF AIR FOR DETERMINATION OF BCME USING THE G.C. DERIVATIVE AND THE G.C.-M.S. TECHNIQUES (DERIVATIVE-G.C.)

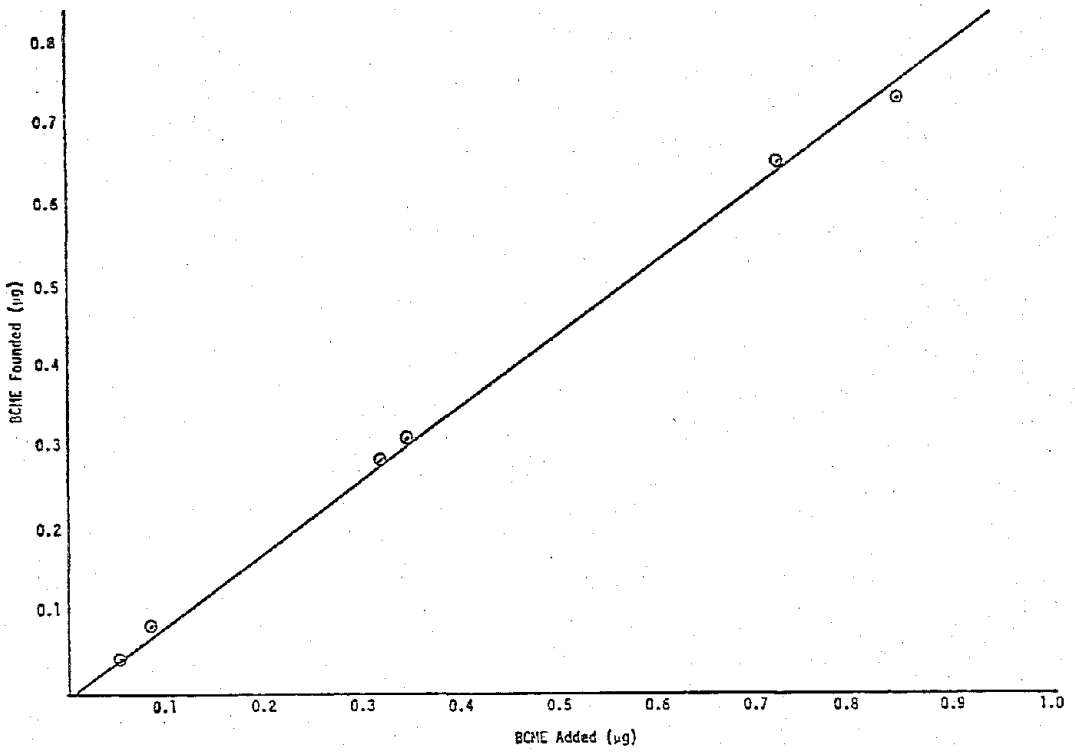


FIGURE 26. RECOVERY OF BCME FROM PREPARED GAS STANDARDS (10 LITERS N_2) USING OPTIMIZED REAGENT

was then made of the data in Table IV [19], indicating an obvious improvement in its linearity and substantiating the needlessness of the excess sodium methoxide. The statistically determined slope is 0.87, indicating no improvement in recovery.

Decision was therefore tentatively made to use the derivative technique for monitoring BCME during the on-site workplace survey. Equipments were thus readied for field application.

At this time, the same chemist of Dow Chemical Company announced the isolation, from the same derivatization solution, of a new symmetric derivative, $Cl_3C_6H_2OCH_2OCH_2OC_6H_2Cl_3$, in addition to the old unsymmetric derivative, $Cl_3C_6H_2OCH_2OCH_2OCH_3$, by using a different

G.C. column. [20] The old unsymmetric derivative was now characterized as no longer specific. In other words, it would give a positive result without BCME ever being present. Thus, all their experiments which gave positive responses for the old unsymmetric derivative of BCME previously, but failed to give response for the new symmetric derivative, were declared BCME-free. The nonspecificity of the old unsymmetric derivative was attributed to the culprit, chloromethylal, $ClCH_2OCH_2OCH_3$, which supposedly would react with the derivatizing agent to form the old unsymmetric derivative. No evidences, however, were offered for the actual existence of chloromethylal or its formation in the environment. No recovery percentage of the new symmetric derivative was mentioned in the cited paper [20]. On the chromatogram, both the new and the old peaks appear to be similar in size. Since 82 to 100 percent of recoveries were obtained for the old unsymmetric derivative, a similar recovery percentage could be roughly assumed for the new symmetric derivative. Thus, as a quantitative tool, it would be facing an arithmetic dilemma of 164 to 200 percent recovery, unless all or most of the old derivatives were not derived from BCME.

By this time, the survey team and the mobile laboratory were already on the road. A new G.C. column was hurriedly made, the detail of which is still covered by the existing secrecy agreement between Dow Chemical and The Bendix Corporation. On trying the new technique with known samples, no expected peak was visible.

A quick phone call was made to the inventor. He commented that the proprietary technique of making the column was quite critical. He was therefore invited to bring his own G.C. column to the mobile

laboratory and apply his expertise. He labored a full day in the mobile laboratory on location, but failed to bring out the elusive peak. He then attributed the failure to the gas chromatography unit on hand.

Since the old derivative G.C. technique caused no difficulties, a quick decision was thus made. The old derivative - G.C. method was to be used as a qualitative pre-test. When, and only when, positive results were obtained in the pre-test, would the G.C.-M.S. method be called upon as a final arbitrator.

E. Adsorber - Mass Spectrometry

Adsorber - mass spectrometry [21] utilizes an enriching adsorber Porapak Q to adsorb the organic compounds from a volume of air. The adsorbed compounds are then thermally eluted into the reservoir of a high-resolution mass spectrometer. It is capable of measuring BCME at 0.1 ppb level in air containing other organic compounds. This method makes use of high-resolution mass spectroscopy and is of high specificity and sensitivity, but suffers, as any other methods involving mass spectrometry, the same disadvantages of high initial cost and the requirement of expertly trained personnel. Furthermore, the delicacy of the instruments precludes their use in a mobile laboratory of a survey team.

F. Adsorber - G.C.-M.S.

The adsorber - G.C.-M.S. is the ultimate technique, with unquestionable specificity and high sensitivity. BCME may be determined at 1 ppb [22] and can even extend to 0.1 to 0.01 ppb [23] levels.

This method was therefore adopted as the ultimate arbitrator. All the survey samples which gave a positive response for BCME in the screening pre-test were to undergo this final confirmation. As a matter of fact, some survey samples which gave negative responses for BCME by the derivative-G.C. pre-test also underwent this confirmatory step.

XVIII. EXPERIMENTAL

A. Kinetic Experiments of BCME Formation in the Gas Phase

The apparatus for following the kinetics of BCME formation in the gas phase is shown in Figure 27. A glass reactor containing a magnetic stirring bar was enclosed in a constant-temperature chamber with ± 1° C accuracy. An accurately weighed portion of paraformaldehyde was introduced into the reactor before all the connections were made. The reactor was then evacuated and heated to the specific reaction temperature and kept there with constant stirring until all the paraformaldehyde completely depolymerized, usually over the weekend. A predetermined amount of dried hydrogen chloride, obtained from the drying setup, described in Paragraph C and shown in Figure 28, was injected into the reactor by means of a gastight syringe, followed immediately by a calculated amount of dry nitrogen to bring the internal pressure of the reactor up to the atmosphere. Thereafter, samples of 100 µl size were periodically withdrawn with a gastight syringe with a 6-inch, 18-gauge needle, which was kept at the reactor temperature in an oven. After insertion, the needle was allowed to remain in place for a couple of minutes before the plunger was withdrawn, lest the formaldehyde polymerize and plug the syringe needle. The withdrawing of the plunger was accomplished in a single stroke without pumping action to avoid time delay, cooling effect, and localized pressure increase, all of which could have caused formaldehyde polymerization.

The samples were analyzed by G.C. for formaldehyde contents as described in Paragraph D.

B. Kinetic Experiments of BCME Formation in the Condensed Phase

The apparatus for following the kinetics of BCME formation in the condensed phases (polar and nonpolar) is shown in Figure 29. The reactions were carried out under nitrogen atmosphere and the reactor was immersed in a constant-temperature bath with ± 0.01° C accuracy.

First, solutions of formaldehyde and of hydrogen chloride in the same dried solvent were separately prepared and kept at the same specific temperature for at least an hour before use. Their methods of preparation are discussed in Paragraphs E and F.

Calculated amounts of these two solutions were introduced under nitrogen into the reactor in sequence. It was essential, however, that the hydrogen chloride solution was added before the addition of the formaldehyde solution, with stirring. Otherwise, an instant polymerization of formaldehyde and precipitation as paraformaldehyde would have resulted. Samples were then taken periodically by opening stopcocks B and C and a stream of reaction solution subsequently flowed out automatically by the siphon action. Portions of the mid-stream were collected in 2-ml vials, and aliquots (1 to 5 µl) of the solution were quickly injected onto a set of columns for analyses of formaldehyde contents as described in Paragraph D. This indirect sampling method was dictated by the necessity of maneuvering in the limited space of an enclosure.

C. Drying of Hydrogen Chloride

The drying setup (Figure 28) comprises a supply cylinder of hydrogen chloride, a 1-foot stainless steel drying column packed

with 100 ml alumina, a glass "tee" with a septum on the side arm, a flowmeter, and a check valve. The hydrogen chloride was allowed to bleed through the drying column about 100 ml per minute. The check valve was partially filled with enough mineral oil to seal the central tube. A gastight syringe was inserted into the hydrogen chloride stream through the septum and the plunger was withdrawn slowly so that the mineral oil level in the check valve was never allowed to go down below the tip opening of its central tube; thus, the hydrogen chloride gas was isolated from air contamination. The withdrawn dried hydrogen chloride of calculated amount was then injected into the gas reactor.

D. Preparation of Hydrogen Chloride Solutions in Organic Condensed Phases

The apparatus for the preparation of solutions of hydrogen chloride in methylene chloride, as well as in carbon tetrachloride, is shown in Figure 30. A three-necked, 1-liter round-bottom flask was equipped with a mercury-sealed stirrer, a vent valve, and a fritted gas inlet tube. The gas inlet tube was connected to an alumina drying tube which, in turn, was connected to the hydrogen chloride supply cylinder. The flask was filled three-quarters full with appropriate solvent, which had been kept in contact with alumina for several days before use.

Hydrogen chloride was admitted slowly through the gas inlet tube and bubbled into the solvent at ambient temperature with constant stirring for about an hour. The solution was then transferred into an amber bottle and kept at the reaction temperature for the particular experiment. The concentration of this solution was

determined immediately before use by extracting 2 ml aliquots with 2 ml portions of water and titrating with 0.5 N standardized sodium hydroxide solution to the phenolphthalein end point, using microburettes.

E. Preparation of Formaldehyde Solutions in Organic Condensed Phases

The apparatus for preparation of solutions of formaldehyde in methylene chloride, as well as in carbon tetrachloride, is shown in Figure 31. A three-necked, 1-liter round-bottom flask was equipped with a mercury-sealed stirrer, a vent valve, and a plain gas inlet tube which was connected to a gas bubbler. The central tube of this bubbler was connected to a copper-tubing-coil heat exchanger.

Enough powdered paraformaldehyde was placed inside the bubbler, but below the tip of the central tube.

The bubbler, with its content and the copper coil was altogether immersed into a mineral-oil bath and heated to approximately 160° C. A slow but steady stream of dry nitrogen was admitted through the heat exchanger carrying the thermally depolymerized formaldehyde into the appropriate solvent in the three-quarters-full flask under constant agitation at ambient temperature. (These solvents had been kept in contact with alumina for several days before use.) After approximately an hour, the solution was transferred to an amber bottle and kept at the reaction temperature of the particular experiment. The concentration of this solution was determined immediately before use by the spectrophotometric method. [24]

This method involved a reaction of formaldehyde in 4 µl samples in 4 ml water, and 0.1 ml of 1 percent chromotropic acid in the presence of 6 ml concentrated sulfuric acid to form a purple monocationic chromogen. The absorbance of the colored solution was read in a spectrophotometer "Spectro-20" at 580 nm, and was proportional to the quantity of formaldehyde in the solution, which could be read directly from a calibration curve.

F. Determination of Formaldehyde Content by G.C.

For the studies of both the gas phase and the condensed phases formation of BCME, the determinations of formaldehyde content were carried out by gas chromatographic analyses. The column set consisted of a 2-inch section of 1/8-inch stainless steel tubing packed with Carbosieve B, followed by a 3-foot section of 1/8-inch stainless steel tubing packed with 100 to 120 mesh Porapak T. The thermal conductivity detector was used for detection purposes. The operating parameters are: Column: 2-inch by 1/8-inch stainless steel Carbosieve B, 120 to 140 mesh, plus 3-foot by 1/8-inch Porapak T, 100 to 120 mesh, at 95° C; detector: thermal conductivity at 200° C; current: 250 ma; carrier: helium; flow rate: 30 ml/min.; inlet temperature: 140° C. Preceding each and every injection of samples, the column set had to be conditioned by an injection of 1 µl of 1 percent formalin solution. The repetitive preconditionings were essential for the accuracy of the chromatogram responses.

G. Analysis of BCME by Direct G.C. Method

BCME in organic solvents such as pentane, hexane, benzene, and toluene was determined by G.C. using a 4-foot by 1/8-inch stainless steel column packed with 0.4 percent Carbowax 1500 on Carbopack A at 95°, and electron capture detector at 220° C. Baseline setting was 150; carrier gas: nitrogen; flowrate: 30 ml per minute; inlet temperature: 140° C.

H. Analysis of BCME by Derivative Method

The BCME in the air was trapped in the derivatization solution in an impinger by means of a monitoring pump. Alternatively, it was first trapped on an adsorber and then thermally flashed into the derivatization solution. To the solution, 5 ml 2N sodium hydroxide was added, the solution was extracted with hexane, and an aliquot of hexane was injected on a G.C. column of 6 feet by 1/4 inch, packed by Dow Chemical proprietary method, at 95° C, with an electron capture detector at 240° C, using current of 37×10^{-7} ma, nitrogen carrier gas, a 50 mm/min flowrate, and inlet temperature at 140° C.

I. Instruments and Reagents

Gas chromatograph -- Bendix 2600 equipped with a thermal conductivity detector, flame ionization detector, and an electron capture detector.

Spectrometer -- Bausch Lomb "Spectro-20"

Bis(chloromethyl) ether -- from Andrulis Research Corporation

BCME permeation tube -- from Metronics Associates, Inc.

Chromotropic acid (disodium salt) -- from Eastman Kodak Company

2,4,6-Trichlorophenol -- recrystallized by Dow Chemical Company

Paraformaldehyde -- from Eastman Kodak Company

s-Trioxane -- from MCB

Formalin -- from Mallinckrodt

Chlorosulfonic acid -- from Mallinckrodt

Methylene chloride -- from Mallinckrodt

Carbon tetrachloride -- from J. T. Baker Chemical Company

Pentane, spectro-grade -- from Mallinckrodt

Hexane, nano-grade -- from Mallinckrodt

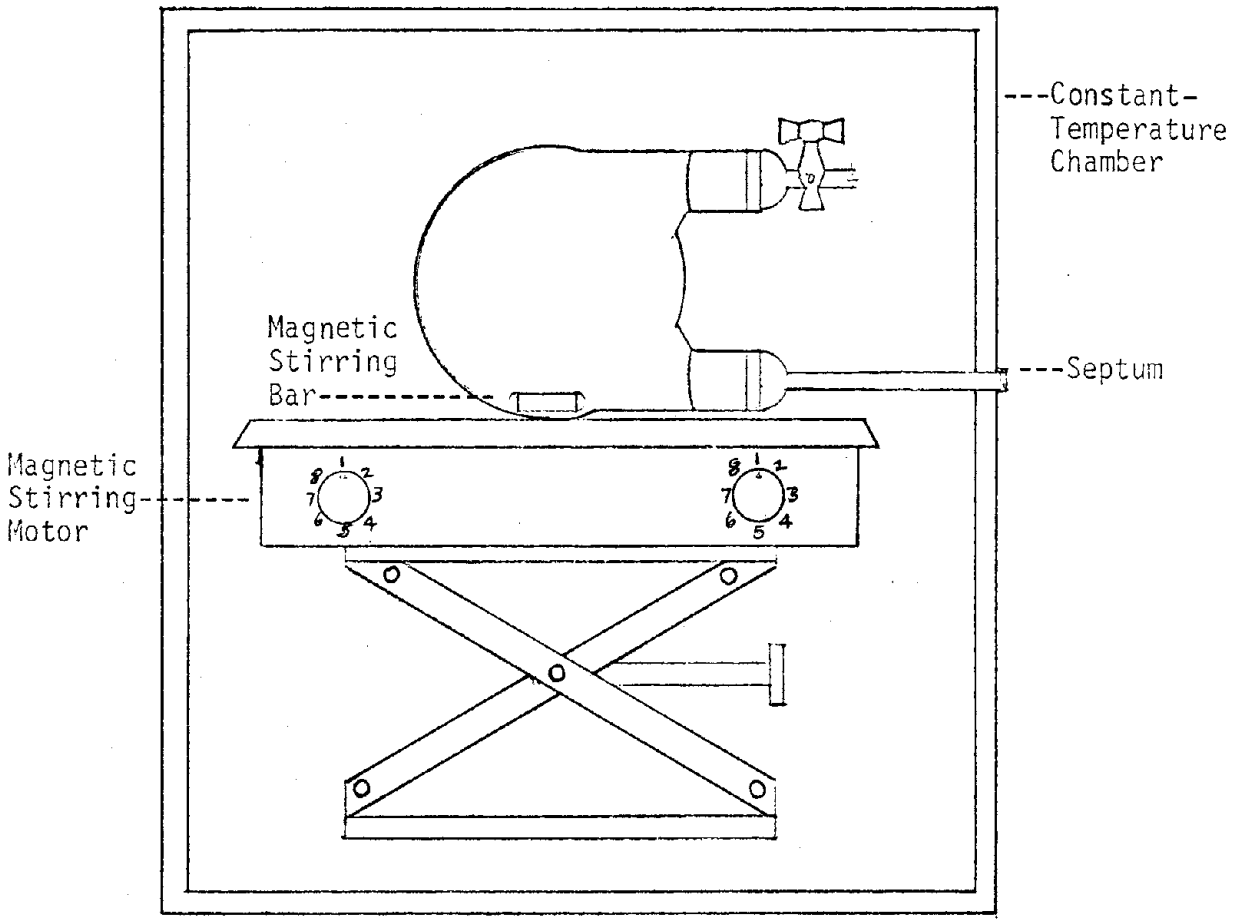


FIGURE 27. GAS PHASE REACTION APPARATUS

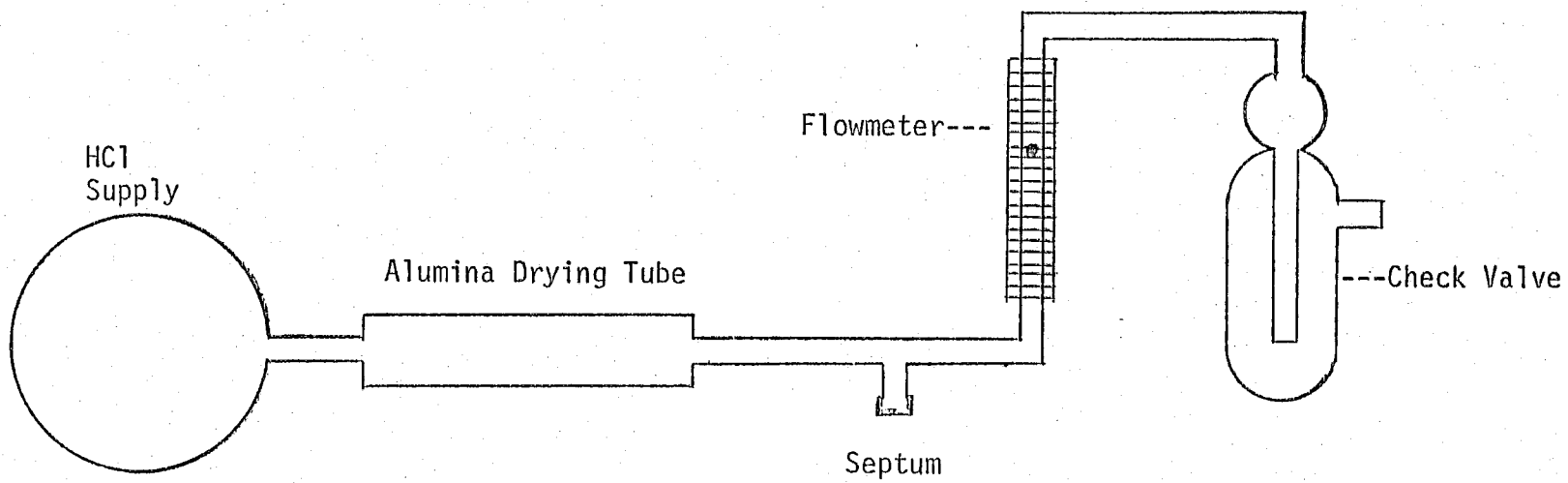


FIGURE 28. HYDROGEN CHLORIDE DRYING APPARATUS

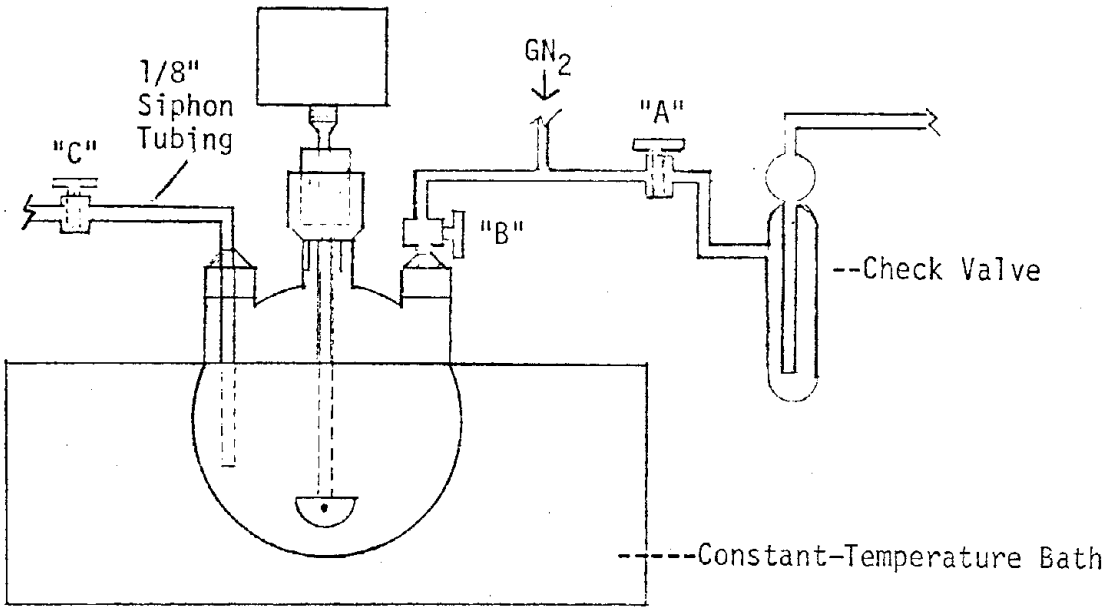


FIGURE 29. LIQUID PHASE REACTION APPARATUS

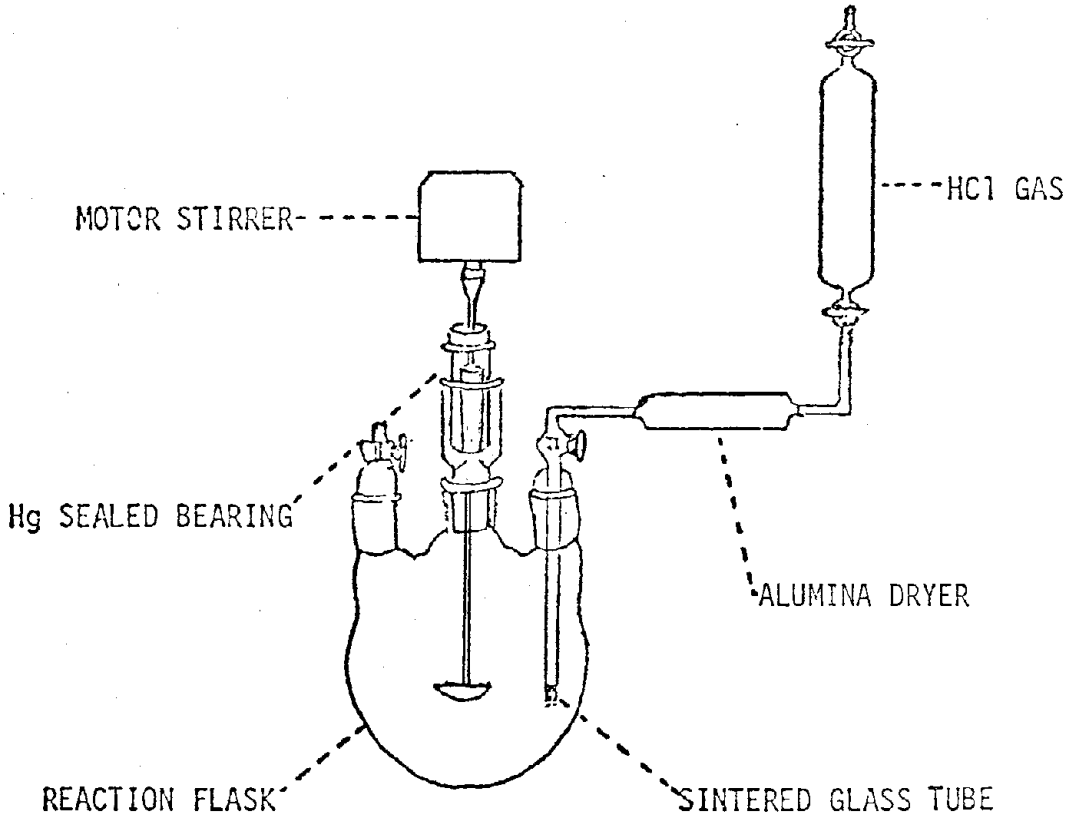


FIGURE 30. HYDROGEN CHLORIDE SOLUTION PREPARATION APPARATUS

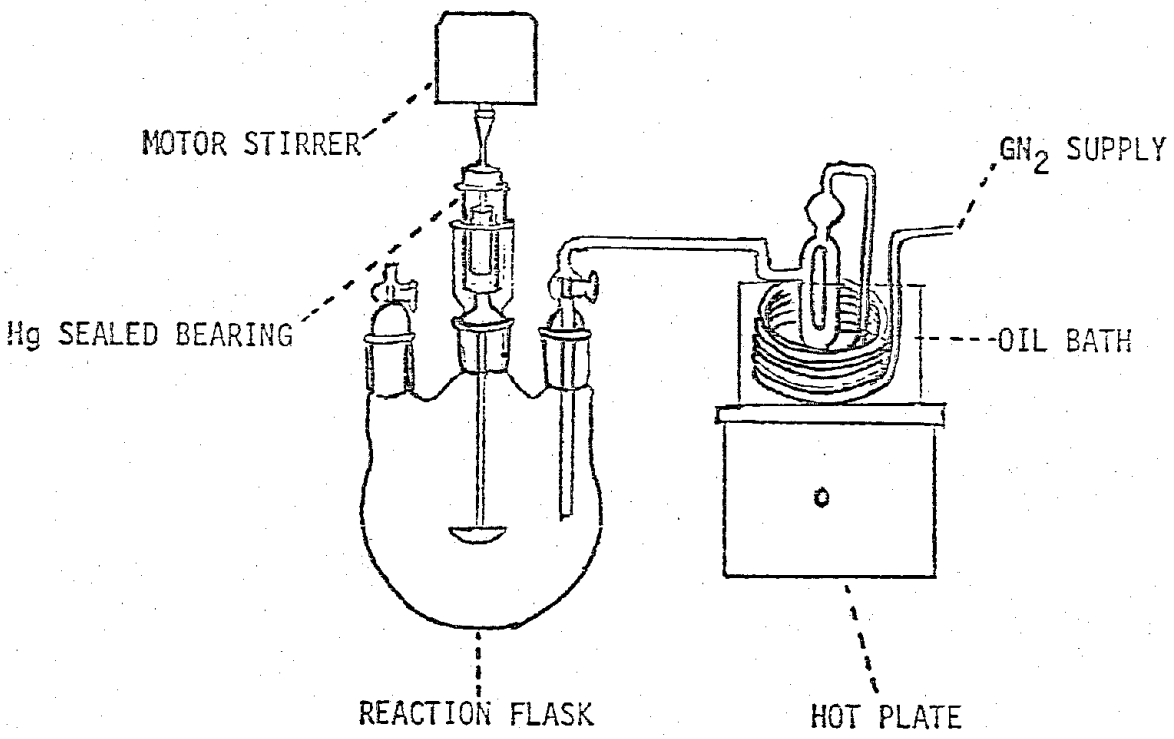


FIGURE 31. FORMALDEHYDE SOLUTION PREPARATION APPARATUS

PART II

INDUSTRIAL HYGIENE SURVEY

XIX. INTRODUCTION

The role of bis(chloromethyl) ether (BCME) in the work environment was considered significant if it formed spontaneously from formaldehyde and chloride ions. This study examined that possibility from two different standpoints: from that of the kinetics and reaction mechanisms involved in the formation of BCME, to that of the actual field survey of workplaces where formation of BCME was considered likely. Task II of the report reflects the findings of the field survey.

BCME is an established carcinogen. Studies by several groups had established a connection between the exposure of laboratory animals to BCME and cancer, [2,5,6,25] where it was shown that carcinomas had resulted from both subcutaneous injections and respiratory insults.[2,5,6,25] A similar response was demonstrated in epidemiologic studies in man. Workers who industrially produced BCME were shown to have a significantly higher incidence of respiratory cancers when compared with "normal" populations. [6,26] Since 1974, when OSHA developed and promulgated standards for BCME, little BCME had been commercially produced; thus, worker exposure was considered minimal. However, if formation of BCME was possible under ambient conditions from small concentrations of formaldehyde and chloride ion, the possibility existed that a considerable portion of the work force were unknowingly being exposed to this active carcinogen.

Thus, the determination of BCME formation in the work environment was of paramount importance. To accomplish this, a first step was to select those work environments which exhibited the best potential for possible BCME formation. Extensive sampling was conducted for BCME and those substances and parameters which were considered influential in allowing or inhibiting its formation.

XX. SAMPLING SITE SELECTION

A. Criteria for Selection of Selected Work Environments

In choosing the industrial processes or work environments to be sampled as part of this project, four criteria were used: (1) The work environment's potential for BCME formation as dictated by the chemical components utilized; (2) numbers of workers exposed; (3) representativeness of the plant to the industry in which it is classified; and (4) the ability or ease of measuring and ascertaining contributing factors to BCME formation.

The first criterion was further subdivided into the following headings: (1) selection of previously identified areas of BCME formation; (2) selection of work environments which exhibit high potential for formation, based on available kinetic and reaction mechanism studies; and (3) selection of work environments which have the known presence of the components which are felt to be needed in BCME formation.

The first criterion and its three subdivisions were also to screen out those processes where more attention and more careful study would be required.

B. Target Industrial Processes

The selection of target industrial processes was begun with two which were known to yield BCME. One of these was the production of chloromethyl methyl ether (CMME), where BCME existed an an impurity. The other was textile manufacturing. Since the CMME process had been extensively investigated by Rohm and Haas and others [6], further work on this process was not considered warranted. In textile manufacturing, some investigators, including Marceleno and Bierbaum, had

conducted preliminary investigations where BCME was detected in the low ppb range. [9] These results were found in areas where free formaldehyde-containing resins were used with magnesium chloride catalysts for wrinkle-resistant finishes. But, because the results proved to be unreproducible, more in-depth investigation was considered necessary not only in textile manufacturing, but also in other industrial work areas where formaldehyde and chloride ions were utilized.

By studying the available kinetics and reaction mechanism data developed to this point, little could be learned which might predispose an industrial process to BCME formation. But because time constraints required that additional kinetics and reaction mechanism work be conducted concurrently with the field survey of work environments, the latter could not be effectively used in the selection of industrial processes which might be predisposed to BCME formation. Thus, the third criterion was most commonly used to identify possible processes where BCME could form.

The two most commonly mentioned components felt necessary for BCME formation were formaldehyde and chloride-containing substances. Formaldehyde is a commonly used organic compound found in many industrial processes. Usually it is found mixed in water, with methanol added as a stabilizer (formalin), or as a polymerized crystalline material (paraformaldehyde). The use of formaldehyde in industry today has special prominence in the production of formaldehyde-containing phenolic and urea resins. This industrial use involves approximately 25 percent of all the formaldehyde produced in the United States. [27]

Chloride-ion-containing substances are almost ubiquitous in industrial processes. Chloride ion is in most water supplies and has recently been detected in trace amounts in airborne hydrocarbon contaminants over major industrial areas. Acids and chemical salts which contain chlorides are commonly used in many industrial processes and may find their way into close contact with formaldehyde in formaldehyde-containing substances. Such processes include the aforementioned resin production industry as well as many other industrial processes.

A review of industrial processes was then conducted to determine which processes utilize both formaldehyde and chloride-containing substances. The industries found in Table 18 are those identified as having sizable quantities of both formaldehyde and chloride-containing substances.

TABLE 18

INDUSTRIES USING FORMALDEHYDE WITH CHLORIDE ION PRESENCE

Types of Industries

Disinfecting
Production of Phenolic Resins
Production of Urea Resins
Production of Melamine Resins
Production of Polyacetyl Resins
Production of Artificial Silk Resins and Cellulose
Production of Dyes
Production of Organic Chemicals
Production of Mirrors
Production of Explosives
Production of Paper
Production of Fertilizers; Urea-formaldehyde
Tanning Hides
Mordanting and Waterproofing Fabrics (textiles)
Improving Latex Qualities
Embalming
Photography
Chrome Printing and Developing
Pesticides
Rendering of Casein, Albumin, and Gelatin Insoluble
Fiberglass Bonding
Adhesive and Laminating Resins; Particleboard
Pathology Procedures

From Table 18, eight processes were chosen and were investigated further as potential industrial processes for study: These include the processes listed in Table 19.

TABLE 19

CRITERIA USEFUL IN THE SELECTION
OF TARGET INDUSTRIES IN BCME FORMATION

1. Known Presence of BCME
   Textiles

2. Presence Indicated by Kinetics and Reaction Mechanism Study
   (Not possible at time of field survey)

3. Components Present Which May Result in BCME Formation
   Production of formaldehyde-type resins and plastics
   Production of dyes
   Production of paper
   Production of fertilizers; urea-formaldehyde
   Photography
   Adhesive and laminating resins; particleboard
   Laboratory operations; embalming and pathology procedures
   Foundries

On November 12 and 13, 1975, a meeting of the BCME Research Project Advisory Committee was convened. This Committee had been formed to assist the NIOSH Project Officer and the contractor as the study was conducted. The main purpose of this second meeting of the Committee was to review selection of target industrial processes, and to recommend those which presented the best possibility for study. As a result, the following industrial processes were chosen for survey.

- Textile Finishing
- Production of Formaldehyde-Containing Resins
- Production of Dyes
- Production of Paper
- Production of Fertilizers
- Use of Laminating and Adhesive Resins (Formaldehyde-Containing) Foundries

Because some members of the Advisory Committee were considered to be experts in the recommended industries, they were asked to nominate potential survey locations, keeping in mind the four criteria for plant selection. As specific companies agreed to the survey, eight sites were chosen which represented the following mix of processes.

- Textile Finishing (2 plants)
- Hospital Procedure Resin Production Laboratory (1 plant)
- Production of Dyes (2 plants)
- Production of Fertilizers (1 plant)
- Foundries (2 plants)

Based on these recommended sites, an itinerary was developed and the actual field study was begun.

XXI. SAMPLING PROTOCOL

A. General Concepts

The guidelines used in the field sampling for this study are described below. They include sampling for BCME and also for other parameters and physical agents which may allow formation of BCME.

The sampling itself was conducted to reflect maximum formation potential, and did not reflect personnel exposures. However, where personnel samples were determined to be useful, they were taken. Yet, due to the nature of the study, determination of actual formation of BCME was paramount, and sampling reflected this concept.

During actual sampling, the processes being studied were run at "normal" conditions. Several batch processes were studied, and, although not continuous, were sampled for as long as possible in their respective operating modes. One "scaled-up" situation in the foundry industry was studied to review several different related processes quickly and easily. All the other processes which were investigated were full-scale operations.

Typically, sampling was conducted during a 1-week period at each site. A mobile laboratory was used for on-site analysis of as many of the samples as possible. The advantages of such an arrangement included rapid analysis and on-site evaluation of samples, thus eliminating the downtime awaiting sample results from the home base laboratory. Additional mobile laboratory advantages are listed in the Appendix. Once sampling was completed, the survey team moved on to the next survey site.

B. Methodologies

Sampling for this study included the following chemical and physical parameters:

1. BCME
2. Formaldehyde
3. Chloride Ion
4. Hydrogen Chloride
5. Metallic Dusts Present
6. Temperature
7. Humidity
8. Atmospheric Pressure
9. Lighting Conditions
10. Air Movement

All of the parameters were measured at each site studied within each industrial process. The following sampling and analytical protocols were used.

1. BCME

Two methods were used to detect BCME concentrations in the work environment. One of these methods served as a screening method whereby positive responses (detectable concentrations) could easily be detected. The second served as a backup sample if positive responses dictated the need for separate analysis and confirmation. This also provided two samples from which qualitative and quantitative results could be compared.

The screening method utilized was the "Dow Method."[19] This method utilized a liquid collection medium which, when coming in contact with BCME, formed a derivative of BCME (phenylate). The

analysis was then conducted for the derivative substance by extracting the derivative into an organic layer and then analyzing the organic layer and derivative by gas chromatography.

The team of researchers at Dow Chemical Company commented on the literature which states that two derivatives are to be found: Derivative A and derivative B. When conducting studies, it was decided to use derivative A. Since derivative A was much easier to work with, using the sampling-analytical systems, it was felt that this derivative was better in view of the problems encountered with derivative B and the gas chromatograph used for this project.

Using the bubbler-pump sampling train at airflow rates of between 0.2 and 1 liter per minute (depending on the pumps used and the specific situations), this method allowed detection of quantities of BCME greater than 0.1 ppb.

The second method of sampling for BCME utilized a sampling train consisting of microreticular porous polymer beads packed into a sampling tube and pump. The analysis of the sample was carried out by thermally eluting the trapped BCME into a gas chromatograph-mass spectrometer system. This analytical method was chosen as the confirmation method largely because of the reliability added by the mass spectrometer.

The sampling tube was a 3-inch by 1/4-inch stainless steel tube packed with 200 mg of 100/120 mesh Porapak Q. Glass wool was used to hold the Porapak Q in place. Each batch of Porapak Q was preconditioned according to manufacturer's instructions; then,

each tube was thermally eluted with nitrogen at 200° C for 30 minutes before use. If a tube sample was not analyzed for BCME content, it was again thermally eluted and reused.

Because of the high pressure drops created by the porous polymer mesh size, sampling rates were low. Typically, they ranged from about 0.05 to 0.2 liter per minute. Also, after initial attempts at using low-flow-rate pumps, larger personnel samplers were required.

Earlier, laboratory testing of the porous polymer tube method was shown to be capable of detecting levels of BCME in the 0.1 ppb range. However, because of the efficiency of the porous polymer tube in collecting and eluting many of the contaminants found in the industrial atmosphere, interferences were commonly encountered. This was partially overcome by using the mass spectrometer to look only at very specific mass/charge numbers.

Sampling tube samples were taken side by side with the "Liquid Derivative Dow Method." Only when BCME was suspected using the "Dow Method" were the tubes analyzed, using the G.C.-M.S. procedure. [23] Sampling tubes were randomly selected and analyzed simply to confirm negative results. Thus, using two methods, the ability to confirm results was possible. This also greatly enhanced specificity, accuracy, and precision in the detection of BCME.

2. Formaldehyde

The "Chromotropic Acid Method" was used to detect formaldehyde concentrations in the workplace environment. However, where

sampling problems were experienced, detector tubes were used, particularly where batch process operations occurred for very short time periods.

The sampling procedure utilized two midget, coarse-fritted bubblers which were connected in series, filled with 1 percent sodium bisulfite, and connected to a sampling pump. A small charcoal-filled tube was placed inline between the bubblers and the pump to protect the pump mechanism whenever high solvent concentrations were encountered. The sampling rate was approximately 1 liter per minute. A portion of the sample was then drawn and analyzed colorimetrically. By comparision with calibration curves, the amount present in the sample was determined, and the airborne concentration calculated. The lower detection limit was typically about 0.1 ppm.

3. and 4. Chloride Ion and Hydrogen Chloride

Three methods were used to measure the chloride ion amount in the work environments. Where possible, total chlorides were measured. A Geomet hydrogen chloride analyzer was used on one occasion to look at long-term hydrogen chloride levels. Also, where needed, detector tubes were used for hydrogen chloride.

The total chloride method used a midget, fritted bubbler-sampling pump sampling train. The collection media was distilled water. Samples collected were analyzed for total chloride content using a specific ion electrode and pH meter. The specific ion electrode was calibrated to detect low ppm levels. Typically, the detection limit for this method was between 0.1 ppm and 1.0 ppm. The most

noticeable interference problem was the collection media's total chloride content. Because sampling was conducted in the mobile laboratory, local distilled water sources were used. Some sources contained less total chloride than others. As a result, sampling detection limits varied slightly from site to site.

Sampling was conducted for 3-hour periods. Flow rates varied slightly but were usually 1 liter per minute.

This system of measuring chlorides did not single out any particular chloride ion source. Since hydrogen chloride is often the suspected hydrogen chloride source, in several instances specific measurements were made for hydrogen chloride or hydrochloric acid mist. One method used was the chemluminescent detection system of the Geomet hydrogen chloride analyzer. This method, with calibration, (used in only one situation) can detect, rather specifically, hydrogen chloride at 0.1 ppm levels. The use of this instrument was limited, however, since it was available only from NASA.

Detection tubes for hydrogen chloride were used when specificity was needed or when sampling problems would not allow the use of the total chloride sampling analysis system. The use of this system typically allowed detection limits of 1 ± 25 percent ppm. Where trace lengths of strain tube discolorations occurred, they were reported as trace amounts present.

Combining these three methods, a reasonable assessment of the amount of chloride ion present was made, both as total chloride and as hydrogen chloride.

5. Dust Concentration (Metals)

The levels of other materials in the atmosphere were also seen as having an impact on the potential for BCME formation. Metallic aerosols were measured to determine their respective roles in potential formation when it was possible for metallic substances to be present. In many instances, by virtue of the processes under study, metallic substances were not sampled.

Samples were taken on filter media (Millipore) by drawing air through the filter at approximately 2 liters per minute. Samples were taken alongside other sampling apparatus for around 3-hour periods.

6. Temperature

Temperature was measured using a calibrated laboratory thermometer. The data were expressed in ^{o}F.

7. Humidity

Relative humidity was ascertained from the individual companies surveyed, utilizing their instruments.

8. Atmospheric Pressure

Atmospheric pressure was ascertained from the individual companies surveyed, utilizing their instruments.

9. Lighting Conditions

No illumination measurements were made. Lighting was simply qualified as to type.

10. Air Movement

Air movement was measured using an Alnor anemometer.

XXII. PROCESSES SAMPLED

A total of eight processes were sampled in this study. Each was unique (including the textile finishing). They are discussed in the following paragraphs.

A. Plant A, Dye Auxiliaries (Resin) Production

1. General

This plant facility was initially constructed for the production of dye materials. Through expansion of the division, the plant had recently undergone a changeover in production to dye auxiliaries which are utilized in placing dyes onto or into various materials. These included various intermediates and resins, most of which had been in production for a year or less. Some strict dye manufacture had continued but was very limited and was being steadily phased out.

In addition to production areas which employed about 20 persons, there was an office, laboratory, and warehouse facility. The facility was separated by a road servicing several other nearby industrial facilities which run through the complex. The road divided the warehousing facility from the production, office, and laboratory areas.

Production of dye auxiliaries was batch-oriented for all product lines. No continuous operations were conducted. Batches ranged from as little as 1,000 pounds to many tons, and required several days for the product to be ready for packing and shipment.

2. Process Used

The process under investigation was the production of a resin

which was used in the dyeing of various paper products. The process involved a relatively simple reaction whereby an amine-formaldehyde resin was produced. A process diagram of this operation is shown in Figure 32.

In this facility, the resin was produced in 3.5-ton batches. The time needed to produce the finished resin was about 24 hours.

Materials were either piped directly into the reaction vessel (formaldehyde, water) or were manually added to the reaction vessel through a small hatch (dicyanamide, ammonium chloride, caustic soda). The step of adding these substances required two employees and about 1/2 hour per batch.

Once the major components were placed into the reaction vessel, mixing, heating, and refluxing took place. This continued for at least 6 hours and usually for about 24 hours. Samples were taken at various times to determine the relative completion of the reaction. Once the laboratory was satisfied with the product, it was then ready for packing. Occasionally, where product specification dictated, water and caustic soda were added to the mixing batch.

The finished product was packed into drums, each containing 400 pounds of the finished resin. This step was done manually by one employee. Resin was piped by gravity flow into a canopy hood, where it was dropped into the drum. The drums were sealed and moved into the warehousing area. The process required about 2 hours per batch.

3. Areas Sampled

Three areas were sampled at this plant. Since the process was essentially a closed-vessel process, only those points involving manual applications required investigation.

The first area measured was the manual addition step where dicyanamide and ammonium chloride were added to the previously charged formaldehyde solution. The reaction vessel hatch was opened and the materials were added in a sequence of 100 pounds of dicyanamide and 50 pounds of ammonium chloride, until 1,500 pounds of dicyanamide were added, resulting in the use of 750 pounds of ammonium chloride. The hatch was then closed and bolted shut. Sampling was conducted around the open hatchway at distances that varied from within the hatchway to 2 feet away.

Exhausts from the closed reaction vessel were also sampled. On the roof, a small, captive scrubber system was installed for this reaction vessel. Effluent from this system was sampled for BCME content at the discharge point.

The last sampling area was in the manual packing area. This was the longest process where the system could be considered open. A canopy hood was in place during the packing procedure. Sampling was conducted around the packing area and within the hood. No sample was taken more than 6 feet away from the spout used in resin delivery; where possible, samples were taken within 2 feet of the packing area.

Two complete batches were sampled at all sampling sites. Sampling was conducted according to the methods outlined in the sampling protocol. No dust sampling was conducted.

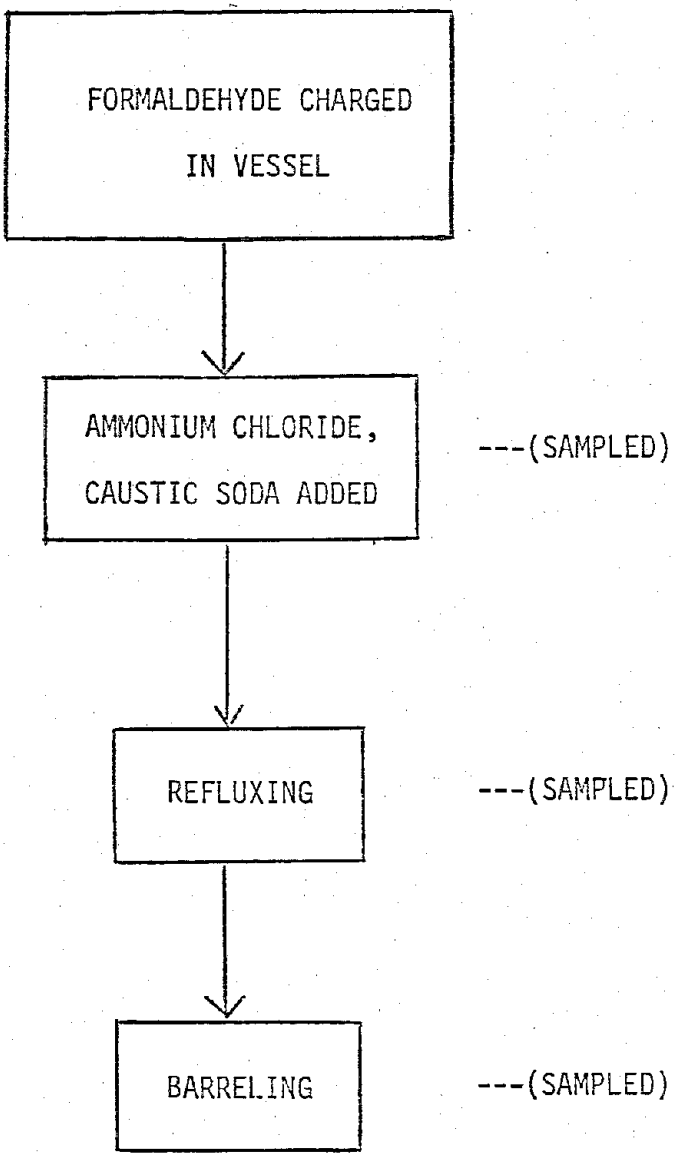


FIGURE 32. PLANT A, DYE AUXILIARIES (RESIN) PRODUCTION PROCESS DIAGRAM

B. Plant B, Dye Manufacturing

1. General

The company surveyed was a producer of dyes and auxiliary chemicals for textiles, paper, and leather products; flavors and dyes for food products; colors for plastics; and other industrially oriented organic chemicals.

The plant sampled was one of the major facilities of several owned by the company. Primarily, it produced dyes which are used in the textile and food industry. Also, it was located next to the research and development center for the company and occasionally was used in "scale-up" operations or actual initial production studies. It was principally for this reason that this plant was surveyed for BCME.

Operations were conducted during three shifts per day, 5 days per week. Two operations were studied. The principal operation and the basic reason for choosing this plant for survey was the production of a yellow-orange dye which required both large amounts of formaldehyde and muriatic acid (dilute hydrochloric acid) in its production. A second operation was also studied but in less detail where waste water (liquor) was treated with formaldehyde and muriatic acid to polymerize any cyanide present.

2. Process Used

a. Yellow-Orange Dye Production - The yellow-orange dye which was produced was essentially based on the aniline molecule, with various substitutions used to develop the proper color in

the dye material. Part of this substitution process required that the amino group be blocked off from reacting while other substitutions were occurring. This was the role of the formaldehyde in this process. Later in the process, muriatic acid was used to remove this blocking group and allow other chemical rearrangement to occur. A process diagram of this operation is shown in Figure 33.

Initially, two tanks were used. In one was mixed formaldehyde, sodium bisulfite, and sulfuric acid. The second tank was filled with an aniline mixture. Both were then dropped into a third tank where they were mixed. An exothermic reaction occurred and to slow the reaction, ice was added and the reaction mixture was cooled to nearly 0° C. The mixture was made alkaline by the addition of caustic soda and was then filtered. The resulting filter cake was reslurred, using water and muriatic acid in excess. Again, the mixture was filtered, and the resulting filter cake reslurred. Muriatic acid and phenol were added and the solution was then refiltered. Once this third filtration was completed, the filter cake was dried in steam-heated ovens, milled, mixed to specifications, and packaged into drums.

The process was a large-volume one where amounts of various materials added sometimes reached into the several-ton category. Most steps in the process required manual addition of materials to the reaction vessels.

To produce this dye, a single batch required up to 4 days to complete the steps necessary to be ready for drying in the oven. Once ready for drying, the dye material was placed into the ovens for several days to ensure complete drying. The material was then stored in drums until sufficient customer demand or warehousing requirements indicated the need for final milling and mixing to customer specifications.

b. Cyanide Liquor Waste Water Treatment - Another dyestuff produced at this plant required the use of large amounts of cyanide-containing materials. As a result of liquor removal, large amounts of the unreacted cyanides were found in the liquor, which presented a serious waste-water removal problem. To reduce the level of cyanide in the waste water to acceptable levels, the cyanide was bound up in a polymer with formaldehyde. To help the reaction occur to sufficient completeness for waste-water requirements, muriatic acid was added to catalyze the reaction.

The reaction was very quick and required little control. All of the operations were closed vessel with only one open point, that where the effluents were dumped into a holding pit, awaiting removal to the disposal point. Addition of chemicals was done by piping needed materials directly into the reaction vessel. No manual work was conducted.

3. Areas Sampled

a. Yellow-Orange Dye Production - Because of the batch nature of this dye production and the relative time required for

production, one batch was followed through from initial mixing to where the process entered the stage where it would be dried. Prior to the drying step, all the formaldehyde was either reacted into the dye or removed in the liquor removal step. No free formaldehyde was present in the dye at the drying step.

Mixing and liquid material addition were conducted in large reaction vessels. Since the process was essentially closed and performed under exhaust ventilation, the only reasonable point of sampling was near the hatchway used for adding material and monitoring the reaction. Depending on the size of the tank, this opening was sometimes as large as 9 square feet. Since this was the only opening, sampling points were set up around and in the hatchway to determine the presence of BCME and its possible formation components. Most sampling points were within 1 to 2 feet from the hatchway. No personnel sampling was conducted. Samples were taken for at least 2 hours, up to about 4 hours maximum. Sampling was keyed to events in the batch being followed. Because of the batch nature of the operation and the needs of sampling, no duplicate samples were taken. To ensure that if BCME was detected, sufficient samples were taken, and several sampling stations were used during each sampling.

No dust sampling was conducted since no metal dusts were used in the process.

Sampling was also conducted at the filter press during the acid filtration step. Again, these samples were area samples.

No personnel routinely worked in the area during the filtration process. Samples were placed both in breathing zone and floor level areas around the filtering process.

b. Cyanide Liquor Waste Water Treatment - Two separate samplings were made of the waste water which contained formaldehyde, muriatic acid, and cyanide liquor. Two samples were taken at the system effluent drop into the holding pit: One above the drop point and one at the downwind edge of the pit. Both were taken during an extended drop of the solution.

A second sampling was made of removing a sample of the effluent from the closed system and analyzing a head sample of the liquid. This procedure was conducted in the laboratory once the effluent sample was drawn and carried into the laboratory.

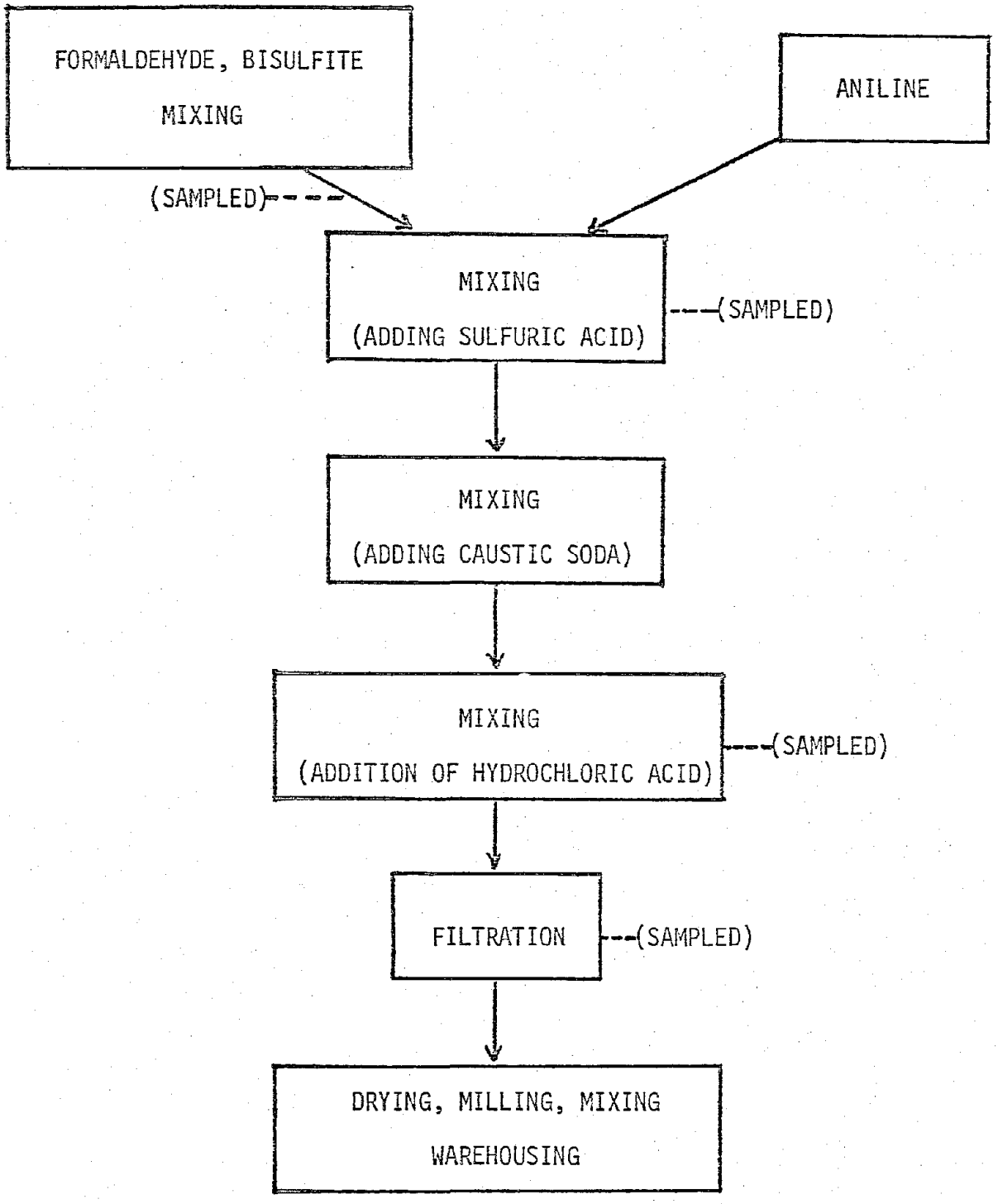


FIGURE 33. PLANT B, DYE MANUFACTURING PROCESS DIAGRAM

C. Plant C, Fertilizer Production

1. General

In this facility, various types of fertilizers were produced. Raw materials were brought to the plant, mixed to either the specifications of the corporation or a large customer, and packaged for shipment to various markets countrywide. The product was formulated at this facility.

A total of about 50 production people worked at this plant during a three-shift-per-day, 5-day work week. Most routine production, packaging, and warehousing were conducted during the first shift. Other shifts were used to monitor operations which could not be stopped for the night.

Recently, production was seriously curtailed due to a lack of demand for fertilizers in this country. The production of the fertilizer in question for this survey was scheduled for only 2 days owing to reduced demand. Most of the production was to go to warehousing rather than directly to consumer markets.

2. Process Used

The product produced which had the best apparent potential for BCME formation was known as 10-6-4 with 60 percent organic material urea-formaldehyde fertilizer. A process diagram is shown in Figure 34. In its mixing process, potassium chloride and urea-formaldehyde were mixed in an acid condition.

To produce this fertilizer, several steps had to be conducted. Initially, the dry ingredients were placed into a hopper where they

were fed into a conveyor at a specified rate based on the specifications of the mix. These ingredients included potash, phosphorus-containing material, limestone, and anhydrous ammonia. Once mixed, the dry materials were ground up and further mixed. They were then placed into an ammoniator. Here, the dry mixture was coated with a mixture of urea-formaldehyde resin (in liquid form) and sulfuric acid.

At this point, the reaction occurred which converted the mixture of products into product which will allow a balanced discharge of nutrients once placed on the lawn or garden. The reaction was exothermic, creating heat of about 200° F in the mixture. Because of the water and liquid present, the fertilizer took a granular form.

Before the fertilizer was ready for packaging, it first had to be dried to remove the available liquids present, then cooled to approximately room temperature, and sized to the proper granular size for proper application characteristics in the home or garden. This operation was conducted in two large rotary drums. The dryer was oil-fired to temperatures over 200° F. Once through the dryer, the fertilizer was moved into the cooler where it was subjected to a flow of cool air. The fertilizer was then sized and either reground to proper size (in the case of too-coarse granules) or reintroduced into the ammoniator for agglomeration (in the case of too-fine granules).

Once delivered from the sizing area, the finished fertilizer was moved into bulk storage. From start to finish, the process was rapid, with total residence time of 30 minutes or less.

A total of three employees were needed to conduct the process. A crane operator was needed for moving dry materials into the mixing containers and removing finished product to bulk storage. Another operator was responsible for the proper mixing of the dry ingredients in the dry area. A third operator worked near the ammoniator to control liquid material flows, reaction temperature, dryer temperature, and product sizing operations. Occasionally, others were needed, particularly during initial startup operations. Also, laboratory technicians were present to take samples of the mixture for quality control purposes.

The areas where the potash-containing chloride ion and the urea-formaldehyde resin made contact were essentially closed and ventilated. One exception existed where the material left the ammoniator exit and fell, by gravity, into the dryer. From this point on to the opening where the cooler fed the sizing, the operation was also closed.

3. Areas Sampled

Sampling was concentrated around several operations: Ammoniator entrance, ammoniator exit, dryer entrance, ammoniator control room, and cooler exit. It was in these areas where the potential for BCME formation was felt to be highest. In all of these areas, personnel were either directly involved in the contact of the urea-formaldehyde resin and potash, or very nearly so, such as in the case of the ammoniator control room.

Samples were area samples. Where possible, several samples were taken of breathing zones. However, most were taken in areas where

the formation potential of BCME was expected to be high. The ammoniator exit was felt to be the most important of those areas since it was the exit for the material immediately after the urea-formaldehyde-potash contact had occurred.

Because of cold weather, the sampling procedures had to be changed to allow use of larger battery-containing pumps. The sampling for BCME was conducted using larger pumps. Formaldehyde and chloride ion sampling continued according to the previously described procedure, but for a 3-hour sampling period.

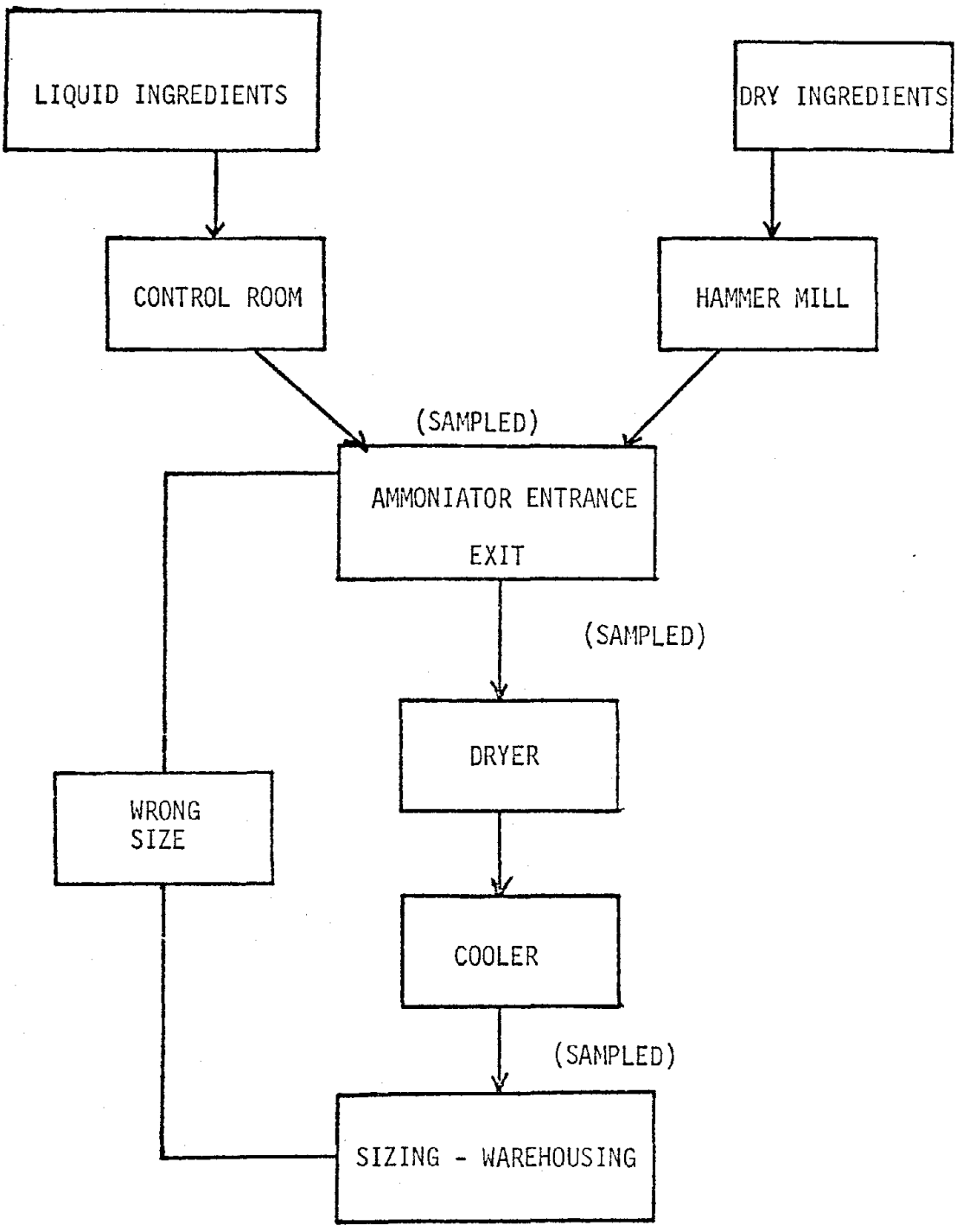


FIGURE 34. PLANT C, FERTILIZER PRODUCTION PROCESS DIAGRAM

D. Plant D, Textile Finishing (Woven Goods)

1. General

This finishing plant was part of the division of this company which produces furniture and drapery fabrics which later become the upholstery and draperies sold on the commercial market.

The process of interest for this survey was the resin-finishing operation. One of the more commonly used finishes was glyoxal urea-formaldehyde, a resin with good qualities for crease prevention. To catalyze the resin into the cloth, magnesium chloride was sometimes used. The containment of the free formaldehyde content of the resin mixture with the chloride content of the catalyst yielded conditions which could have proved influential in the possible formation of BCME.

Resins were used on 2 of the 10 finishing frames located within the plant. In the immediate area around these two frames, there were about five to six employees. Because the frame was located centrally in the plant, many other employees commonly passed through this area during the normal course of their daily activities. This was probably the area where the largest number of employees were present in the plant at any one time.

Operations were usually conducted at the plant three shifts per day, 5 days per week. Since production had been curtailed somewhat, only the resin-finishing operation was then operating on the 5-day-per-week schedule.

The process was essentially a continuous one with only minor changes in the process during the course of a shift or working

day. Changes were limited to the type of cloth being finished, the resin content of the solution used to impart the crease-resistant qualities, and the temperature limits of the cloth in the ranges.

2. Process Used

The process to resin-finish textiles was a relatively simple one, but one that had several steps. A process diagram of the material as it was finished is shown in Figure 35.

Initially, the cloth was washed, bleached, dyed, and dried before it was ready for resin finishing. The cloth, usually in a roll, was unraveled into a scray. This unraveling prevented sheaves and rollers in the frames farther down the process line from pulling too hard on the cloth, possibly causing danger to the product. It was then ready for resin treating.

On a mezzanine above the finishing frame floor were vessels which were used to mix the resin solution to the specifications required by the intended use of the cloth. Typically, 200- to 250-gallon batches of glyoxal resin, and appropriate amounts of magnesium chloride, water, softeners, hand builders, and other substances were used to complete the mixture. This solution was mixed and then gravity-fed to the pad bath area as needed.

The cloth was drawn through the pad bath containing the resin solution. The pickup of resins was about 70 to 80 percent of the weight of the cloth. Once through the pad bath, the cloth was squeezed between rollers to eliminate a large amount of the water.

Cloth with 30 percent resin weight was started on a process where it was dried and stretched, and the resin cured. Initially, the cloth was drawn through a predryer. Here, temperatures were sufficiently hot to drive off the water found in the resin mixture, but not so hot as to change the resin mixture. The water acted as a carrier in this process but did not have an actual part in the finished product.

The next step was more drying, but this time while the cloth was being stretched. By the end of this step, most of the water was removed, but nothing had occurred to the resin. Temperatures in the dryer typically reached 250° F.

The last major step in finishing was in the cure oven. Here, the temperatures were elevated to those needed to cure or harden the resin with the catalyst present. These approached 300° F or higher, as needed.

Once curing was completed, the cloth was sent to inspection and on to warehousing for shipment or storage.

Each step listed above had a separate piece of equipment associated with it. All steps from the mixing tank and pad bath to the cure could possibly have had an exposure, since suspected BCME formation components were present in varying degrees.

In this facility, the predryer, dryer, and cure oven were ventilated through enclosures of the equipment. The remaining areas were essentially unventilated, releasing vapors and mists into nearby work environments.

The operation was a continuous one. Cloth was fed continuously into the scray with the exception of stops made for securing a new bolt of cloth to the tail of the preceding bolt, and when the cloth and bath were stopped.

3. Areas Sampled

Sampling was divided into two segments. Initially, screening sampling was accomplished; this was followed by more concentrated sampling at various points which were thought to have high BCME formation potential. This style of sampling could be conducted since the process was continuous and essentially free from major changes day to day.

The initial sampling was conducted at the following sites: Mixing tanks, pad bath, predryer entrance, dryer entrance, dryer exit, cure oven entrance, and cure oven exit. Samples were taken as close as possible to the operations. For example, in the mixing tanks area, the sample was drawn over the top of the open vessel about 6 to 12 feet from the liquid surface when full. In the case of the dryer entrance and exit, samples were taken to the side of the moving cloth about 3 feet from the entrance or exit. All samples were area samples.

The primary purpose of this segment was to screen out the potential areas where the formation potential seemed highest; those areas which resulted in the highest formaldehyde and chloride ion concentrations. Four areas indicated that more concentrated sampling might prove necessary. These included the mixing room, the pad bath, the predryer entrance, and the dryer entrance.

When sampling these four areas, four sampling sites were chosen which covered as many potential formation points as possible. In some cases, this meant taking samples at work stations or at work stops. Alternately, in some cases, this meant surrounding an entrance or piece of equipment with sampling equipment. The hoped-for result was to detect significant amounts of BCME in the finishing process.

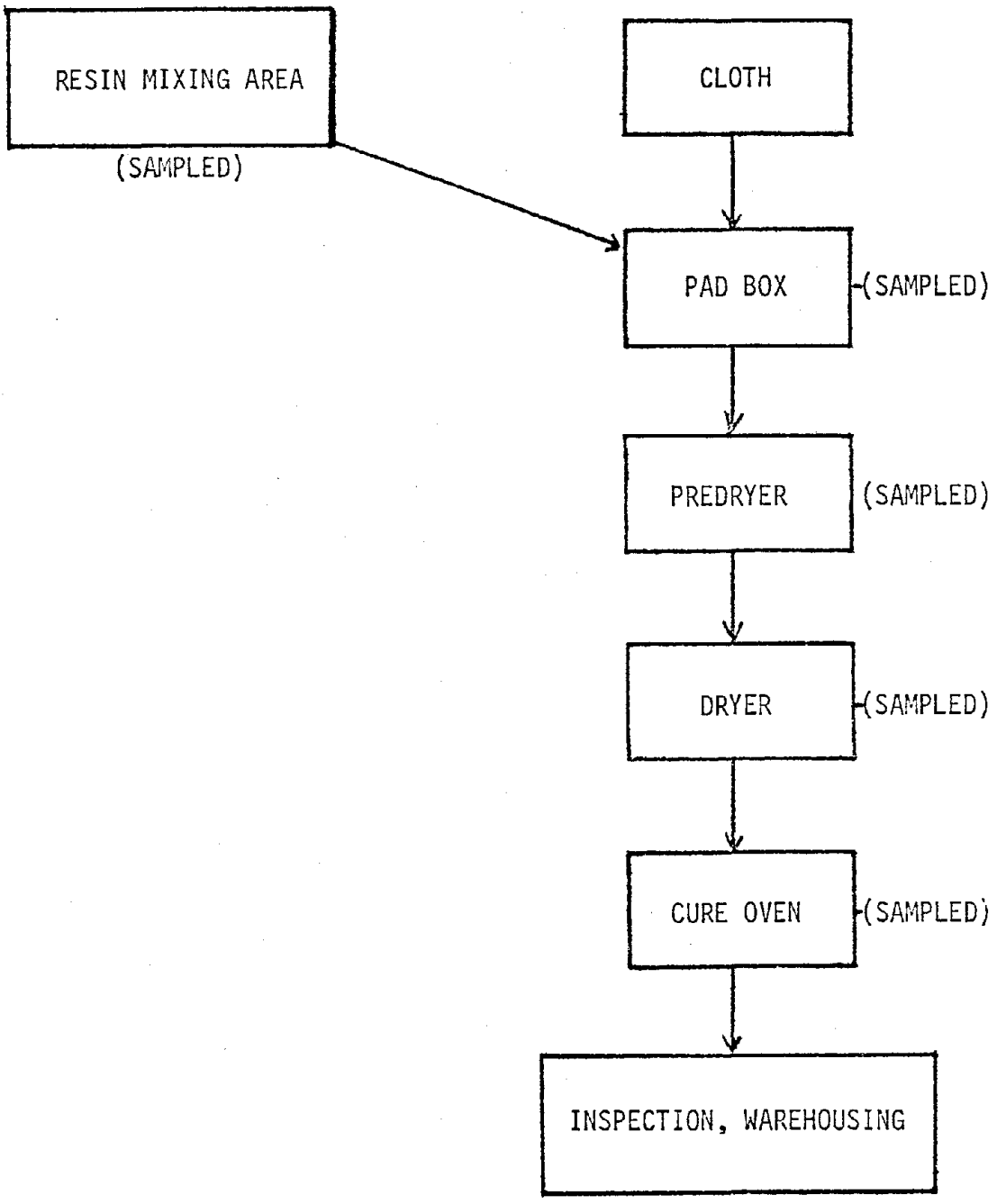


FIGURE 35. PLANT D, TEXTILE FINISHING (WOVEN GOODS) PROCESS DIAGRAM

E. Plant E, Textile Finishing (Knit Goods)

1. General

This plant facility was primarily used in the production of knit goods. These goods included 50 percent dacron, 50 percent cotton blends, and 100 percent cotton goods. Goods were knitted, dyed, and finished to market specifications in this plant. Production at this plant totaled about 400,000 pounds per month.

The area of interest for this project was the finishing area. A total of about 28 employees were present in this area during any shift of the three-shift-per-day, 5-day-per-week schedule. A total of five tubular and three open-width finishing lines were present in this plant.

In the process of interest, finishing, about 90 percent of all the production of this plant was given a glyoxal-urea formaldehyde, magnesium chloride resin finish to improve the wrinkle resistance of the knitted goods. Due to the presence of free formaldehyde and chloride ion in the components present in the resin mixture, a potential for BCME formation was felt to be present.

2. Process Used

The first step in the finishing of knit goods at this plant was the mixing of the resin and catalyst. A mezzanine existed in the center of the finishing room area where the resin, in an aqueous form, was gravity-drawn into mixing vessels. Magnesium chloride was added manually with buckets to the specifications of the mix. Softeners and wetting agents were added as needed. The

batch, about 200 gallons, was then mixed and, within several minutes, was ready for use.

The medium of the resin-catalyst mixture was aqueous. With the addition of the catalyst, the pH of the mixture became slightly acidic with a temperature which was nearly ambient. No pH adjustments were made.

The typical mixes of the resins were from about 200 pounds resin/ 40 pounds catalyst to 100 gallons of water to about 50 pounds resin/10 pounds catalyst to 100 gallons of water.

Once the resin-catalyst mixture was produced, it was used on either one of two finishing lines: tubular knit finishing and open knit finishing. Both employed different finishing techniques, hence they require separate discussions.

In the tubular finishing operation, the knit goods were moved manually to the pad bath area where the knit goods were drawn through a series of stretchers and exposed to steam. Cloth temperatures were between 90° F and 105° F at this point. The cloth was then drawn through the resin bath to about 80 percent w/w wet pickup.

After the resin bath, the cloth was introduced into the predryer stage where some of the aqueous solution was removed. Temperatures in the predryer averaged about 250° F.

Once predried, the cloth was calendered, stretched, and steamed to final dimensions. Then the cloth was introduced into the loop

dryer-curing ovens. At this point, temperatures reached over 300° F for curing of the resin. Again, the residence time was short but was longer than in the drying stages, about 4 minutes. The process was enclosed and ventilated. In this process, with the combination of heat and residence time, the lubricants commonly used in knitting evolved from the knitted cloth as a smoke which was visible in the curing oven.

After the completion of curing, the cloth was ready for inspection and movement into the warehousing area.

The second method for finishing knitted cloth used at this plant was a process known as open-width finishing. Since knitted cloth is produced in a tubular form, the cloth had first to be cut lengthwise and stretched, forming the more normal cloth appearance. The cloth then entered the finishing line.

Initially, the cloth was drawn through the pad box as was the case in the tubular knit process. However, once this was completed, the cloth entered a machine which combined the predryer, dryer, and curing oven into one continuous step. At the end, the cloth was ready for inspection and removed to the warehouse. The machine was commonly known as a tenter frame or more simply "frame."

The temperature gradient in the one-step process began at approximately 250° F and rose about 100° F before the curing was completed. Although these temperatures were somewhat higher than those found in the tubular finishing process, the residence time was reduced by one-half to one-quarter of that required in the tubular finishing.

No changes were needed in resins or other conditions present in the finishing process for open width.

A process diagram of this finishing operation is shown in Figure 36.

Ventilation was present in some of the process areas. It was very important in the dryer-cure oven steps where temperatures had to be carefully controlled while evolving vapors and mists were removed. At these points, ventilation appeared to be adequate. In other areas such as the mixing mezzanine and the pad box areas, no controls existed. As a result, formation potentials for BCME were higher in these uncontrolled areas.

3. Areas Sampled

Because of the nature of the equipment in use in this facility, the intent was to sample as many areas as possible with the several processes where formation of BCME was possible. With two separate production operations going on simultaneously, this made the task more difficult. Once the sampling had been conducted in all areas, those which were felt to have the highest potentials were to be sampled more closely.

Area samples were taken nearby (within several feet) of the following production steps: Mixing mezzanine, pad box, predryer entrance, predryer exit, precalender, loop dryer-cure oven entrance, and loop dryer-cure oven exit. This was conducted , where applicable on both the tubular and open-width finishing lines. No attempt was made to take personnel samples.

Sampling was conducted for periods of about 3 to 4 hours.

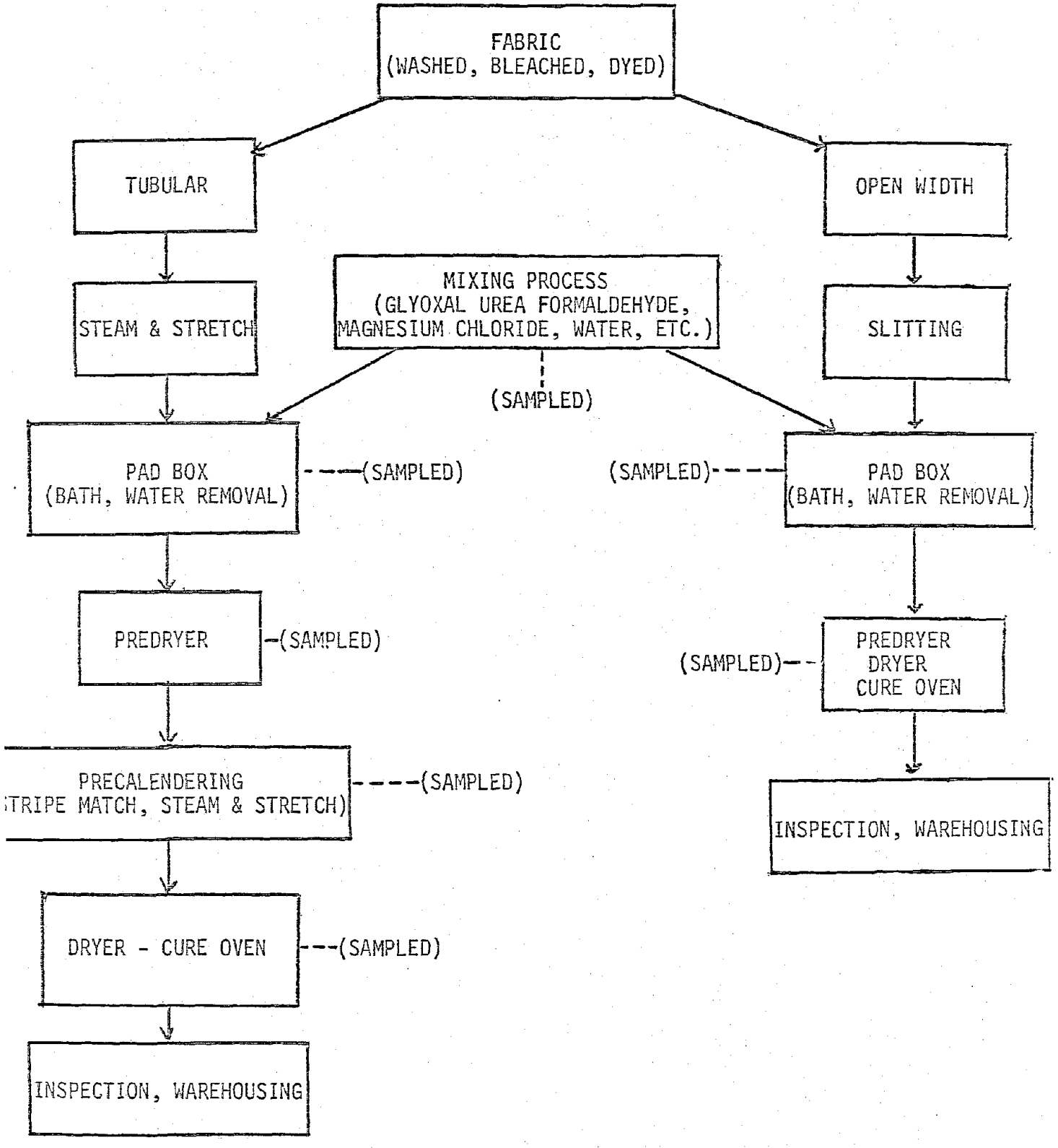


FIGURE 36. PLANT E, TEXTILE FINISHING (KNIT GOODS) PROCESS DIAGRAM

F. Plant F, Hospital Procedures (Resin)

1. General

This facility was a laboratory operation which was used in conjunction with a burn center of a major armed forces hospital. The role of the laboratory was one of support in all phases of biochemical analysis and support functions. Included in the support function was the occasional production of "gel pads" which were used for supporting burn patients. The production of such pads was limited to about 4 weeks per year, in which about 20 to 40 pads were produced. This was essentially a batch process.

About 10 people were employed in the laboratory area. Several others were employed in the building but were located in separate sections of the facility. Approximately one-half of the staff was military. The remaining were civilian and were divided between technical personnel and support (maintenance) personnel.

In the process of interest, two people were employed to produce a gel resin from polyvinyl alcohol, formaldehyde, hydrochloric acid, and water. Food dyes were also added to provide color for identification and aesthetic purposes.

2. Process Used

The product of this process was a gel pad which was used in the treatment of burn victims. Because of the plastic properties of the gel, it was exceptional in allowing burn victims to rest body weight on sensitive tissue comfortably without hindering the healing process. Because the gel pad was not presently available from commercial sources, this laboratory was charged with the

production of these pads for use in the burn ward of the hospital.

The process required to make this product was very much batch-oriented. A typical batch yielded one large pad and several small pads, and required about 5 days of processing. The process required the following procedural steps (a process diagram is shown in Figure 37).

Approximately 3,500 ml of deionized water was placed into a stainless steel container which was placed into a hot water bath set to approximately 90° C. Before the deionized water was heated significantly, 400 grams of polyvinyl alcohol were added, and the mixture was slowly stirred. When the initial charge of polyvinyl alcohol was almost completely dissolved, another 500 grams of polyvinyl was added. This charge was added to 1,600 ml of cold water and was then added to the heated mixture slowly while it was being stirred.

The mixture was stirred for 2 to 3 hours while it was heated. When the solution became clear, the mixture was ready for the next step.

Up to this point, one person was required. Most of the operations were essentially monitoring. No environmental controls were used.

The hot, clear mixture was then taken off the water bath and moved into a hood. With stirring, 4 pints of formalin solution (37 percent formaldehyde), 24 ml of hydrochloric acid, and food coloring were added. This was done as quickly as possible with a fast stirring rate. Once these items were added and the food color

appeared to be evenly mixed, the mixture was placed into a large, flat-bottomed, olive oil-coated pan. The pan was covered with plate glass and placed into an oven set to 71° C. The gel pad was cured for 2 to 2-1/2 hours. Upon removal, the pad was placed into a large pan containing cool tap water. Water from the tap was circulated through the pan continuously for 24 hours.

Two people conducted the procedure in the mixing, baking, and rinsing stages. Environmental controls present included only the hood used in mixing and rinsing. The oven was uncontrolled as were aisleways between the hood and oven.

Once the pad had been rinsed for 24 hours, it was moved to another larger rinsing pan where water containing 3 percent urea in propylene glycol was washed over the pad. This was conducted for 3 days. The pads were then dried, cut to size as needed, and heat-sealed in polyethylene bags.

3. Areas Sampled

Three of the procedure steps were sampled for BCME and its possible formation components. These were: (1) The addition of formaldehyde and hydrochloric acid to the heated mixture, (2) residence in the oven baking (curing), and (3) removal from the baking pan. It was felt that these three areas would show the most significant potential for BCME formation.

For the most part, area samples were taken. Some were taken in personnel breathing zones. Two personnel samples were taken. Because of the short sampling periods, formaldehyde and hydrogen chloride concentrations were sampled using detector tubes only.

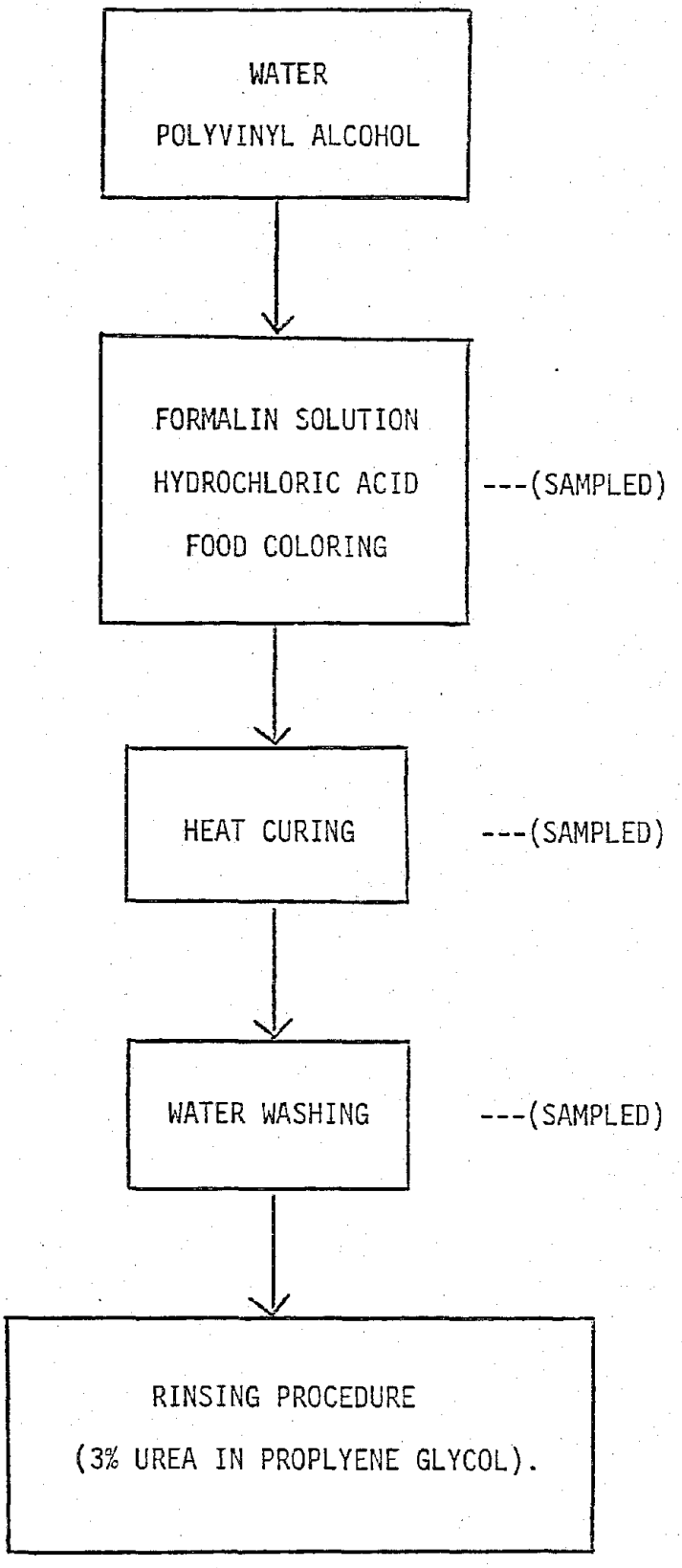


FIGURE 37. PLANT F, HOSPITAL PROCEDURES (RESIN) PROCESS DIAGRAM

G. Plant G - Foundry Products (Research Plant)

1. General

The facility studied was contained in the research and development section of a major producer of foundry products. Contained within the research area was a small foundry which was used for the testing of new foundry products. The foundry also performed development work, with the special customer problems that occur in the foundry industry.

Operations at this laboratory-pilot plant were on a small scale and were therefore usually batch type, such as pouring which requires reheating (melting) before the next batch can be poured. The same applied to coremaking operations which were also under study. However, this did allow better control over study conditions since this was a laboratory-type situation where sampling could be conducted to allow "possible best formation potential" to occur.

Products made in this foundry operation were used for testing purposes. No commercial use of the products was made.

2. Process Used

Two foundry processes were studied in this operation: Coremaking and metal pouring. Both processes were conducted as small-batch operations. A process diagram is shown in Figure 38.

The first process studied was coremaking. Cores are made to provide interior areas within castings. Two types of core materials

were used. The first mixture was of the following blend:

Sand - 100 parts

Phenol-formaldehyde resin - 2 parts

Ammonium chloride catalyst in aqueous media - 0.4 part

These items were blended by machine. The technician then checked the mixture for the proper consistency. Since the resin-catalyst system will "set" with time, the mixture was used immediately.

The coremaking machine was an air-operated press which heated molding materials to temperatures in excess of 500° F. The mixture was blown under pressure into the mold of the press. It was then placed under pressure and heated to 450° F for 1 minute. At the end of 1 minute, the molded cores were removed from the press and allowed to cool. At this point, the resin at the surface of the core was cured. Excess heat retained in the core was dissipated; however, much of it tended to hasten curing of the core's interior. Usually, cooling of a 1-inch by 1-inch by 3-inch core required about 10 to 15 minutes.

Coremaking, using this equipment, was conveniently conducted for about 1 hour.

A second coremaking was conducted using a slightly different mixture of materials. They included:

Sand - 100 parts

Furfuryl alcohol-formaldehyde resin - 2 parts

Ammonium chloride catalyst in aqueous media - 0.4 part

Again, these items were mixed, molded, and cooled under essentially the same conditions as the phenol-formaldehyde resin mixture.

The two resins selected represented the two most commonly used binding resins used in the foundry industry which have both formaldehyde and chloride ions present. The specific resin catalyst systems used were manufactured by the company visited and reflect their particular resin-catalyst formulation.

A second process studied was the metal-pouring area. Molten iron was cast in 2,000-gram molds. The mold was a common step-type mold used to determine the qualities of the binders developed by this company. Two molds were prepared which had used the phenol-formaldehyde, ammonium chloride binder system. Iron was melted and heated to approximately 2,900° F. It was then poured into a preheated ladle, manually moved to the mold, and poured at 2,700° F. The outer casing of the mold was graphite, a substance which was understood to be inert during the pouring.

Once poured, the core was allowed to cool for at least 30 minutes in the mold. The casting was then opened and allowed to air-cool for about 8 hours, at which time it could be handled without protective equipment.

Two pourings were made with the phenol-formaldehyde resin, ammonium chloride catalyst mix.

Later, the furfuryl alcohol-formaldehyde resin, ammonium chloride catalyst mix was used in two pourings of iron. The process was essentially the same as that discussed for phenol-formaldehyde resin mixes.

3. Areas Sampled

Three areas were sampled: two in the coremaking, and one in the metal pouring.

The first area sampled in the coremaking was the molding machine. Samples were taken above it and to the side for BCME and formaldehyde. Because of analytical difficulties, direct-reading detector tubes were used for determination of chloride as hydrogen chloride. Samples for hydrogen chloride were taken at the side of the machine. Dust was sampled above the molding machine.

The other area sampled in the coremaking process was the core cooling area which was several feet away from the core molding machine. Sampling was conducted above and slightly to one side of the cooling cores for BCME, formaldehyde, and hydrogen chloride. Sampling times averaged about 1 hour.

During the coremaking, a large canopy hood was used over the core molding machine. The cooling area was uncontrolled with the exception of general room ventilation.

The sampling took place in the metal pouring area. Once the metal was poured (10 seconds), sampling over and beside the graphite mold began. The sampling conducted over the mold was accomplished with a hood that covered the mold.

Additional sampling was conducted in the same area, beside the outer covering of the graphite mold. Any effluent from the mold not captured in the hood was sampled by this means.

Sampling times were about 1 hour per resin system and included two metal pourings. Sampling was all area sampling.

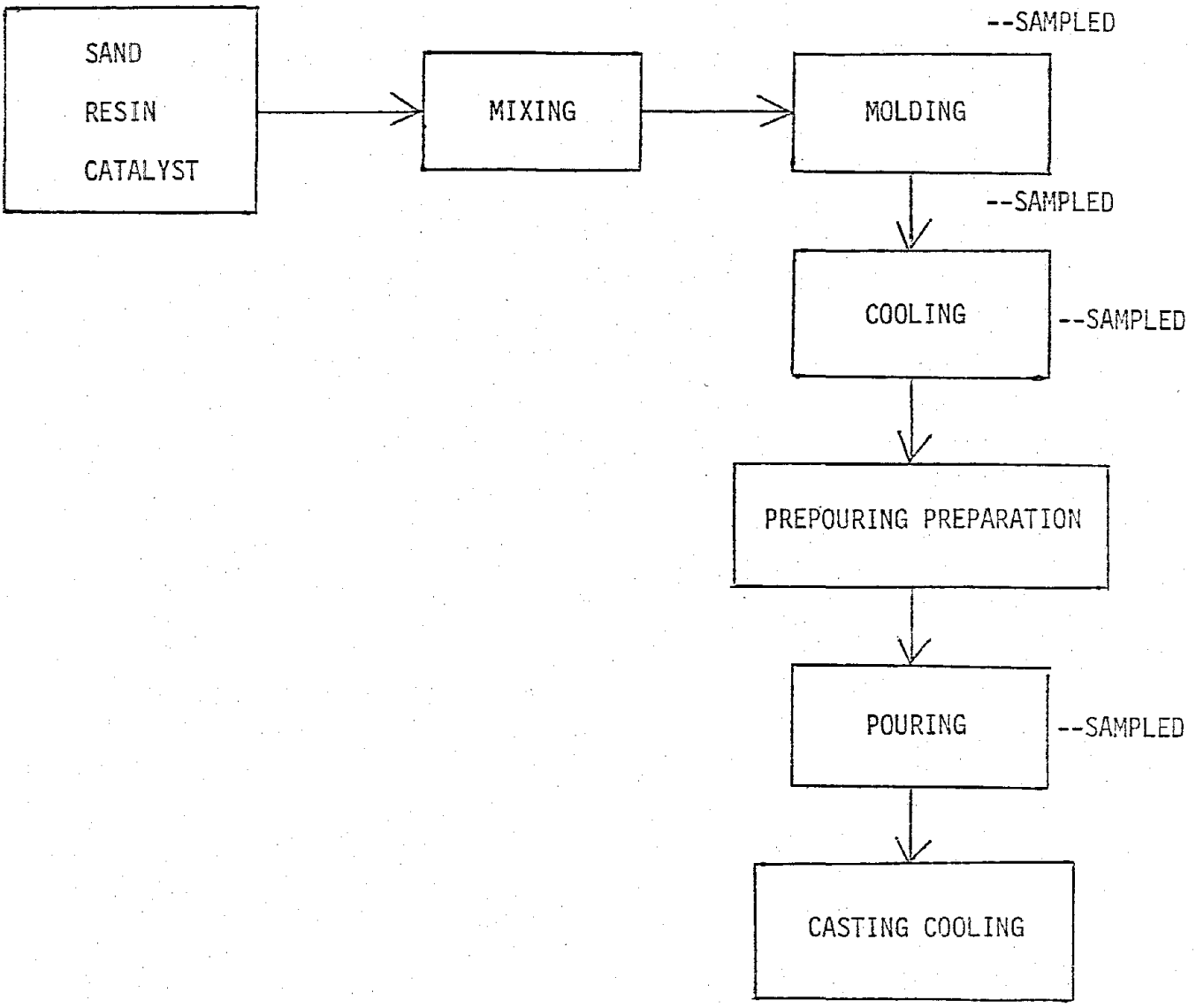


FIGURE 38. PLANT G, FOUNDRY PRODUCTS (RESEARCH PLANT) PROCESS DIAGRAM

H. Plant H, Foundry Products (Full-Scale Plant)

1. General

The plant facility under study was a producer of metal castings. Both ferrous and nonferrous metals were cast in this shop. The company which ran this facility was headquartered on-site and did not have any other facilities.

The production areas included a pattern shop, a pattern storage area, cold and hot box molding areas, a pouring department (which included several areas), a finishing shop, and a scrap metal storage area. In addition, other areas included the headquarters office areas, sales department, engineering department, and laboratory facilities.

This foundry poured castings which weighed from several ounces to about 1,500 pounds. Usually, castings were in the 50- to 500-pound range due to furnace sizes and facility limitations. Fifty to 100 castings were made of one item at one time. Mold production and pouring were conducted in two daily shifts during a 5-day work week.

During full production, a total of about 150 people were employed in production areas, with another 40 to 50 working in other plant areas.

2. Process Used

The process in question was the production of ferrous metal castings, using shell molds. The molds were formed using heat and a catalyst to cure the resin/sand mixture. Once cooled and hardened, metal was poured into the molds, allowed to cool, and then

removed from the mold. A process diagram is shown in Figure 39.

The molding department received a molding sand which was premixed. The components of this mixture included sand, phenol-formaldehyde resin, and hexamethylenetetramine. The hexamethylenetetramine was used as a high-temperature catalyst for the curing of the resin. The sand mixture was forced around a metal pattern, pressed into place, and then heated to about 400° F. The total time involved in this process was about 1-1/2 minutes.

The mold was then removed, broken in half, and both halves glued together. The result was a completed mold commonly called a "shell mold" in this facility.

Molds were moved into the pouring area. Some molds were simply placed in a sand pit, located centrally in the facility, and poured. No control over effluents from pouring were in use. However, this method was used only in small-job pouring of molds of this type. Castings were cooled in the same area.

In a second-type pouring, a cooling range was used. Metal was poured under a slotted hood and then the castings were moved into the cooling range which was ventilated.

Because of the smaller size of the castings, cooling usually required only a few hours. Castings were then manually broken out or shaken out of the molds and moved to the finishing area for welding, grinding, cleaning, etc.

The whole process, from mold making to being ready for finishing, was accomplished in 2 days.

3. Areas Sampled

Three areas were sampled during this study: Mold production, open pouring, and cooling range pouring. During all sampling, conditions and parameters were essentially uniform.

Sampling was conducted around the molding area. Especially, samples were taken above and below the heat-curing area, at the gluing area, and at the control panel for the molding operation. All samples were taken within a circle of about 15 feet in diameter. During operations where metal was poured into the molds on the floor, samples were taken at the nearest structural columns or nearby equipment. Because the area was open where pouring was conducted, some of the sampling points were as far as 20 feet from the nearest mold. Sampling in this area continued until molds were broken and castings moved to the finishing area.

When samples were taken during pouring using the cooling range, they were taken in the hood area of the range (just beside the pouring), at the range exit, and back away from the entrance where workers stood during pouring. Again, sampling was continued until the castings had cooled.

All sampling was area sampling. Sampling methods varied slightly in that detector tubes were used to determine the presence of formaldehyde and hydrogen chloride.

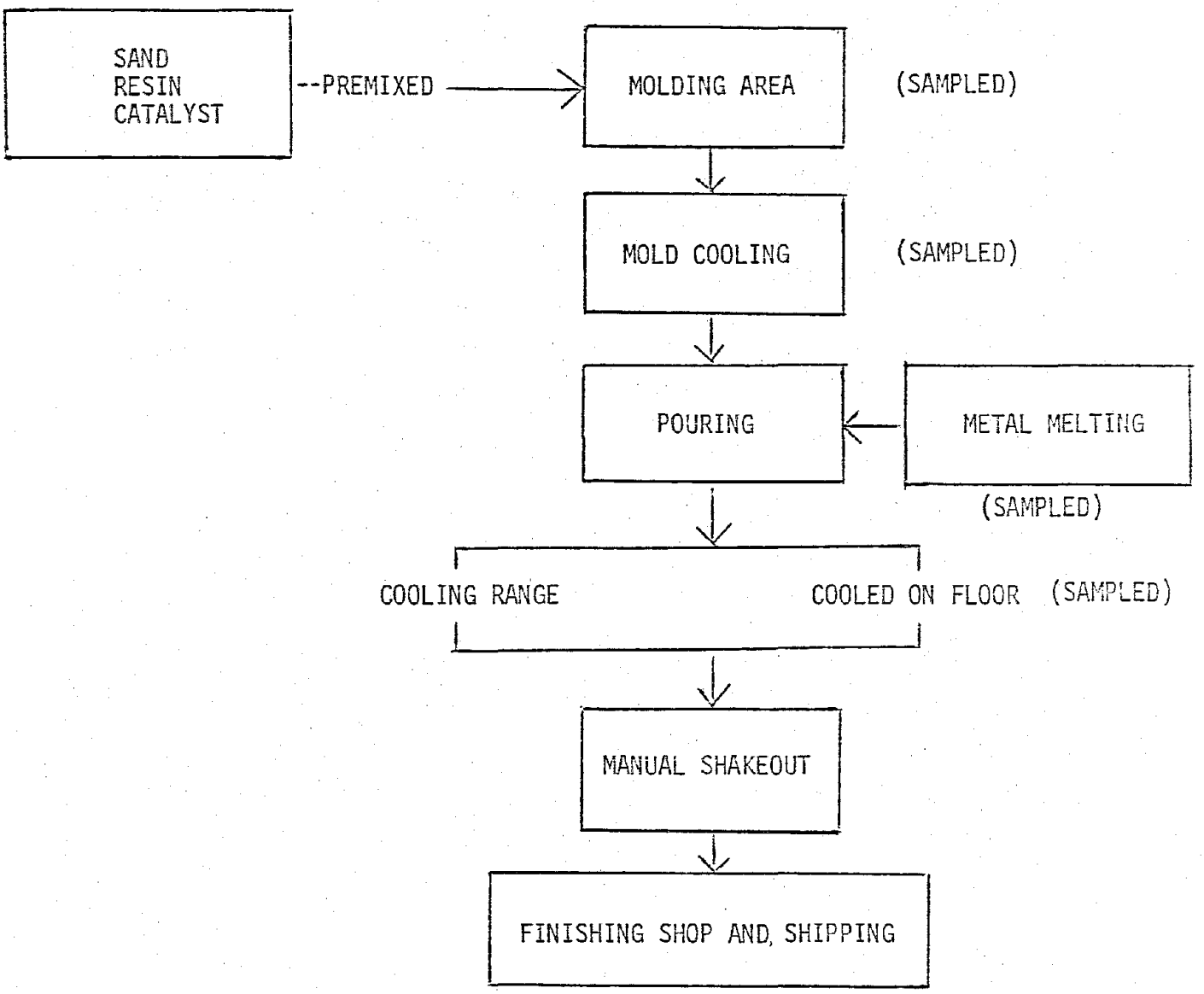


FIGURE 39. PLANT H, FOUNDRY PRODUCTS (FULL-SCALE PLANT) PROCESS DIAGRAM

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APPENDIX

BCME SAMPLING RESULTS

BCME SAMPLING RESULTS

PLANT A

PRODUCT DYESTUFFS AUXILIARY (RESIN)

Sample Location	Sample #	Date of Sample	BCME Sample Tube #	Sample Volume	Result (PPB)	BCME Sample Derivative	Sample Volume	Result (PPB)	CH_2O Concentration	Cl Concentration	Temperature	Relative Humidity	Pressure	Lighting	Air Movement
Mixing Tub	77	2/24/76	8	45.6ℓ	N/A	#32 LD(A)	25.7ℓ	< 0.2ppb	1.9ppm	3.3ppm	66°F	41%	760mm	Incandescent Window Sunlight	<50 fpm
Mixing Tub	78	2/24/76	18	57.0ℓ	N/A	#10 LD(A)	26.3ℓ	< 0.2ppb	1.0ppm	1.5ppm	66°F	41%	760mm	Incandescent Window Sunlight	<50 fpm
Mixing Tub	79	2/24/76	28	45.6ℓ	N/A	# 3 LD(A)	28.2ℓ	< 0.2ppb	1.1ppm	4.5ppm	66°F	41%	760mm	Incandescent Window Sunlight	<50 fpm
Mixing Tub	84	2/25/76	50	27.0ℓ	N/A	#32 LD(B)	10.3ℓ	< 0.2ppb	0.8ppm	< 1.0ppm	81°F	26%	760mm	Incandescent Window Sunlight	<50 fpm
Mixing Tub	85	2/25/76	9	18.8ℓ	N/A	#10 LD(B)	10.8ℓ	< 0.2ppb	1.9ppm	1.8ppm	81°F	26%	760mm	Incandescent Window Sunlight	<50 fpm
Scrubber Exit	80	2/24/76	32	32.4ℓ	N/A	#42 LD(A)	17.3ℓ	< 0.2ppb	< 0.1ppm	1.0ppm	42°F	58%	760mm	Sunlight	200 fpm
Scrubber Exit	86	2/25/76	13	11.7ℓ	N/A	# 3 LD(B)	9.5ℓ	< 0.2ppb	< 0.1ppm	< 1.0ppm	68°F	30%	760mm	Sunlight	200 fpm
Scrubber Exit	87	2/25/76	4	11.1ℓ	N/A	#42 LD(B)	7.6ℓ	< 0.2ppb	< 0.1ppm	< 1.0ppm	68°F	30%	760mm	Sunlight	200 fpm
"Pack Out", Barreling	81	2/25/76	19	38.4ℓ	N/A	#32 LD(A)	14.4ℓ	< 0.2ppb	< 0.1ppm	1.7ppm	61°F	50%	760mm	Incandescent Window Sunlight	<50 fpm
"Pack Out", Barreling	82	2/25/76	11	24.4ℓ	N/A	#10 LD(A)	14.1ℓ	< 0.2ppb	< 0.1ppm	1.7ppm	61°F	50%	760mm	Incandescent Window Sunlight	<50 fpm

BCME SAMPLING RESULTS

PLANT A PRODUCT DYESTUFFS AUXILIARY (RESIN)

Sample Location	Sample #	Date of Sample	BCME Sample Tube #	Sample Volume	Result (PPB)	BCME Sample Derivative	Sample Volume	Result (PPB)	CH_2O Concentration	Cl^- Concentration	Temperature	Relative Humidity	Pressure	Lighting	Air Movement
"Pack Out", Barreling	83	2/25/76	3	17.7ℓ	N/A	# 3 LD(A)	14.6ℓ	< 0.2ppb	0.2ppm	2.6ppm	61°F	50%	760mm	Incandescent Window Sunlight	<50 fpm
"Pack Out", Barreling	88	2/26/76	48	59.2ℓ	N/A	#32 LD(A)	33.6ℓ	< 0.2ppb	0.3ppm	< 1.0ppm	64°F	48%	760mm	Incandescent Window Sunlight	<50 fpm
"Pack Out", Barreling	89	2/26/76	41	63.5ℓ	N/A	#10 LD(A)	28.7ℓ	< 0.2ppb	< 0.1ppm	< 1.0ppm	64°F	48%	760mm	Incandescent Window Sunlight	<50 fpm
"Pack Out", Barreling	90	2/26/76	21	39.3ℓ	N/A	# 3 LD(A)	32.0ℓ	< 0.2ppb	< 0.1ppm	< 1.00ppm	64°F	48%	760mm	Incandescent Window Sunlight	<50 fpm

BCME SAMPLING RESULTS

PLANT B PRODUCT DYESTUFFS

Sample Location	Sample #	Date of Sample	BCME Sample Tube #	Sample Volume	Result (PPB)	BCME Sample Derivative	Sample Volume	Result (PPB)	CH_2O Concentration	Cl^- Concentration	Temperature	Relative Humidity	Pressure	Lighting	Air Movement
First Tub (Mixing)	57	2/17/76	46	61.0ℓ	N/A	#32 LD(A)	27.4ℓ	< 0.1ppb	5.8ppm	2.0ppm	71°F	52%	760mm	Incandescent Window Sunlight	120 fpm
First Tub (Mixing)	58	2/17/76	42	63.5ℓ	N/A	# 3 LD(A)	32.7ℓ	< 0.1ppb	0.7ppm	2.6ppm	71°F	52%	760mm	Incandescent Window Sunlight	120 fpm
First Tub (Mixing)	59	2/17/76	35	63.5ℓ	N/A	#10 LD(A)	29.3ℓ	< 0.1ppb	2.2ppm	1.4ppm	71°F	52%	760mm	Incandescent Window Sunlight	120 fpm
Second (Aniline Addition)	60	2/17/76	8	66.6ℓ	N/A	#10 LD(B)	48.2ℓ	< 0.1ppb	< 0.1ppm	0.7ppm	78°F	32%	760mm	Incandescent Window Sunlight	70 fpm
Second (Aniline Addition)	61	2/17/76	3	65.7ℓ	N/A	# 3 LD(B)	50.5ℓ	< 0.1ppb	0.3ppm	0.7ppm	78°F	32%	760mm	Incandescent Window Sunlight	70 fpm
Second (Aniline Addition)	62	2/17/76	12	108.5ℓ	N/A	#32 LD(B)	53.5ℓ	< 0.1ppb	0.3ppm	0.9ppm	78°F	32%	760mm	Incandescent Window Sunlight	70 fpm
Second (HCl Addition)	63	2/18/76	11	99.2ℓ	N/A	#32 LD(A)	56.2ℓ	< 0.1ppb	< 0.1ppm	0.3ppm	70°F	47%	760mm	Incandescent Window Sunlight	180 fpm
Second (HCl Addition)	64	2/18/76	19	246.0ℓ	N/A	#10 LD(A)	56.4ℓ	< 0.1ppb	< 0.1ppm	< 0.1ppm	70°F	47%	760mm	Incandescent Window Sunlight	180 fpm
Second (HCl Addition)	65	2/18/76	16	73.5ℓ	N/A	# 3 LD(A)	60.2ℓ	< 0.1ppb	< 0.1ppm	< 0.1ppm	70°F	47%	760mm	Incandescent Window Sunlight	180 fpm
Samples	66 -	69 were	lost.												

BCME SAMPLING RESULTS

PLANT B PRODUCT DYESTUFFS

Sample Location	Sample #	Date of Sample	BCME Sample Tube #	Sample Volume	Result (PPB)	BCME Sample Derivative	Sample Volume	Result (PPB)	CH_2O Concentration	Cl^- Concentration	Temperature	Relative Humidity	Pressure	Lighting	Air Movement
Filter Press	70	2/19/76	4	177.0ℓ	N/A	#32 LD(A)	38.3ℓ	< 0.1ppb	< 0.1ppm	0.9ppm	70°F	44%	760mm	Incandescent Fluorescent	100 fpm
Filter Press	71	2/19/76	50	63.1ℓ	N/A	#10 LD(A)	40.7ℓ	< 0.1ppb	< 0.1ppm	1.3ppm	70°F	44%	760mm	Incandescent Fluorescent	130 fpm
Filter Press	72	2/19/76	9	70.8ℓ	N/A	# 3 LD(A)	42.1ℓ	< 0.1ppb	< 0.1ppm	1.8ppm	70°F	44%	760mm	Incandescent Fluorescent	70 fpm
Filter Press	73	2/19/76	13	53.1ℓ	N/A	#42 LD(A)	34.6ℓ	< 0.1ppb	< 0.1ppm	0.7ppm	70°F	44%	760mm	Incandescent Fluorescent	200 fpm
Second Tub (Diazotization)	74	2/20/76	21	166.0ℓ	N/A	#32 LD(A)	37.2ℓ	< 0.1ppb	< 0.1ppm	0.8ppm	75°F	28%	760mm	Incandescent Window Sunlight	170 fpm
Second Tub (Diazotization)	75	2/20/76	48	82.0ℓ	N/A	#10 LD(A)	36.7ℓ	< 0.1ppb	< 0.1ppm	0.6ppm	75°F	28%	760mm	Incandescent Window Sunlight	170 fpm
Second Tub (Diazotization)	76	2/20/76	41	48.6ℓ	N/A	# 3 LD(A)	40.1ℓ	< 0.1ppb	< 0.1ppm	0.9ppm	75°F	28%	760mm	Incandescent Window Sunlight	170 fpm
Waste Water Treatment								< 0.1ppb							
Waste Water Treatment								< 0.1ppb							
Waste Water Treatment								< 0.1ppb							

BCME SAMPLING RESULTS

PLANT C PRODUCT FERTILIZER PAGE 1 of 2

Sample Location	Sample #	Date of Sample	BCME Sample Tube #	Sample Volume	Result (PPB)	BCME Sample Derivative	Sample Volume	Result (PPB)	CH_2O Concentration	Cl^- Concentration	Temperature	Relative Humidity	Pressure	Lighting	Air Movement
Ammoniator Entrance	48	2/5/76	50	29.8ℓ	N/A	# 3 LD(A) #11 LD(A)	20.4ℓ 14.1ℓ	< 0.1ppb < 0.1ppb	0.2ppm	1.6ppm	41°F	29%	760mm	Incandescent	<50 fpm
Ammoniator Entrance	50	2/5/76	21	17.4ℓ	N/A	# 3 LD(B)	36.3ℓ	< 0.1ppb	0.7ppm	3.0ppm	42°F	55%	760mm	Incandescent	<50 fpm
Ammoniator Exit	46	2/5/76	48	2.8ℓ	N/A	#32 LD(A) #16 LD(A)	18.6ℓ 12.6ℓ	< 0.1ppb < 0.1ppb	0.2ppm	2.8ppm	43°F	28%	760mm	Incandescent	150 fpm
Ammoniator Exit	51	2/5/76	46	18.0ℓ	N/A	#32 LD(B)	60.0ℓ	< 0.1ppb	1.1ppm	7.1ppm	42°F	62%	760mm	Incandescent	250 fpm
Ammoniator Exit	52	2/5/76	15	55.5ℓ	< 0.1ppb	#32 LD(C)	12.8ℓ	< 0.1ppb	0.4ppm	1.8ppm	40°F	59%	760mm	Incandescent	100 fpm
Ammoniator Exit	53	2/5/76	29	54.0ℓ	< 0.1ppb	#10 LD(C)		< 0.1ppb	1.9ppm	4.4ppm	40°F	59%	760mm	Incandescent	50 fpm
Control Room	47	2/5/76	28	18.7ℓ	N/A	#10 LD(A) #12 LD(A)			0.3ppm	8.2ppm	38°F	61%	760mm	Incandescent	<50 fpm
Dryer Entrance	54	2/5/76	7	19.5ℓ	< 0.1ppb	#30 LD(A)	4.4ℓ	< 0.1ppb	0.5ppm	6.3ppm	40°F	59%	760mm	Incandescent	100 fpm
Cooler Exit	49	2/5/76	14	19.5ℓ	N/A	#10 LD(B)	65.0ℓ	< 0.1ppb	1.0ppm	21.2ppm	38°F	57%	760mm	Incandescent	<50 fpm
Cooler Exit	55	2/5/76	6	30.3ℓ	N/A	#12 LD(B)	29.1ℓ	< 0.1ppb	1.8ppm	17.3ppm	38°F	57%	760mm	Incandescent	<50 fpm

BCME SAMPLING RESULTS

PLANT C PRODUCT FERTILIZER PAGE 2 of 2

Sample Location	Sample #	Date of Sample	BCME Sample Tube #	Sample Volume	Result (PPB)	BCME Sample Derivative	Sample Volume	Result (PPB)	CH_2O Concentration	Cl^- Concentration	Temperature	Relative Humidity	Pressure	Lighting	Air Movement
Cooler Exit	56	2/5/76	#13	30.3ℓ	N/A	#42 LD(A)	27.2ℓ	< 0.1ppb	0.9ppm	0.2ppm	38°F	57%	760mm	Incandescent	< 50 fpm

BCME SAMPLING RESULTS

PLANT D PRODUCT TEXTILES PAGE 1 of 3

Sample Location	Sample #	Date of Sample	BCME Sample Tube #	Sample Volume	Result (PPB)	BCME Sample Derivative	Sample Volume	Result (PPB)	CH_2O Concentration	Cl^- Concentration	Temperature	Relative Humidity	Pressure	Lighting	Air Movement
Mixing Area	21	1/27/76	30 39	17.9ℓ 24.4ℓ	N/A N/A	---	---	---	0.5ppm	0.5ppm	73°F	78%	760mm	Fluorescent	<50 fpm
Mixing Area	22	1/27/76	10	11.5ℓ	< 0.1ppb	# 3 LD(A)	44.6ℓ	< 0.1ppb	0.5ppm	0.5ppm	72°F	64%	760mm	Fluorescent	<50 fpm
Mixing Area	29	1/28/76	17	40.5ℓ	(NIOSH)	# 3 LD(A)	---	< 0.1ppb	0.4ppm	0.1ppm	81°F	35%	760mm	Fluorescent	<50 fpm
Mixing Area	32	1/29/76	50	25.0ℓ	N/A	#10 LD(A)	29.1ℓ	< 0.1ppb	0.2p.m	1.1ppm	81°F	38%	760mm	Fluorescent	<50 fpm
Mixing Area	33	1/29/76	35	26.3ℓ	< 0.1ppb	#32 LD(A)	26.8ℓ	< 0.1ppb	0.2ppm	1.1ppm	82°F	42%	760mm	Fluorescent	<50 fpm
Pad Box	18	1/27/76	27 32	38.4ℓ 33.3ℓ	N/A N/A	---	---	---	0.7ppm	0.3ppm	79°F	63%	760mm	Fluorescent	<50 fpm
Pad Box	23	1/27/76	33	59.8ℓ	N/A	#32 LD(A)	13.3ℓ	< 0.1ppb	0.9ppm	0.1ppm	79°F	76%	760mm	Fluorescent	<50 fpm
Pad Box	26	1/28/76	43	26.2ℓ	(NIOSH)	#42 LD(A)	---	< 0.1ppb	0.3ppm	0.2ppm	73°F	32%	760mm	Fluorescent	<50 fpm
Pad Box	34	1/29/76	12	36.1ℓ	N/A	#32 LD(B)	50.1ℓ	< 0.1ppb	< 0.1ppm	< 0.1ppm	80°F	26%	760mm	Fluorescent	<50 fpm
Pad Box	35	1/29/76	42	42.3ℓ	N/A	#10 LD(B)	50.5ℓ	< 0.1ppb	< 0.1ppm	0.1ppm	81°F	27%	760mm	Fluorescent	<50 fpm

BCME SAMPLING RESULTS

PLANT D PRODUCT TEXTILES PAGE 2 of 3

Sample Location	Sample #	Date of Sample	BCME Sample Tube #	Sample Volume	Result (PPB)	BCME Sample Derivative	Sample Volume	Result (PPB)	CH_2O Concentration	Cl^- Concentration	Temperature	Relative Humidity	Pressure	Lighting	Air Movement
Pad Box	36	1/29/76	3	33.8ℓ	N/A	# 3 LD(B)	56.4ℓ	< 0.1ppb	0.8ppm	< 0.1ppb	83°F	34%	760mm	Fluorescent	<50 fpm
Pad Box	37	1/29/76	48	13.7ℓ	N/A	#42 LD(B)	55.9ℓ	< 0.1ppb	< 0.1ppm	0.2ppm	83°F	24%	760mm	Fluorescent	<50 fpm
Predryer Entrance	20	1/27/76	18	38.3ℓ	N/A	----------	-----	-------	0.2ppm	0.3ppm	86°F	46%	760mm	Fluorescent	<50 fpm
Exit			45	45.3ℓ	N/A										
Predryer Entrance Exit	24	1/27/76	30	19.9ℓ	< 0.1ppb	#42 LD(A)	15.7ℓ	< 0.1ppb	0.9ppm	< 0.1ppm	87°F	48%	760mm	Fluorescent	<50 fpm
Predryer Entrance Exit	42	1/30/76	32	22.0ℓ	N/A	#32 LD(B)	41.5ℓ	< 0.1ppb	0.6ppm	0.2ppm	93°F	19%	760mm	Fluorescent	90 fpm
Predryer Entrance Exit	43	1/30/76	18	17.3ℓ	N/A	#10 LD(B)	38.5ℓ	< 0.1ppb	1.3ppm	0.5ppm	96°F	19%	760mm	Fluorescent	150 fpm
Predryer Entrance Exit	44	1/30/76	16	24.5ℓ	N/A	# 3 LD(B)	12.7ℓ	< 0.1ppb	1.3ppm	0.6ppm	96°F	19%	760mm	Fluorescent	150 fpm
Predryer Entrance Exit	45	1/30/76	8	16.1ℓ	N/A	#10 LD(B)	44.8ℓ	< 0.1ppb	0.5ppm	0.1ppm	93°F	21%	760mm	Fluorescent	110 fpm
Dryer (Frame) Entrance	19	1/27/76	16	5.5ℓ	N/A	----------	-------	-------	0.8ppm	< 0.1ppm	86°F	44%	760mm	Fluorescent	<50 fpm
			37	35.1ℓ	N/A										
Dryer (Frame) Entrance	25	1/27/76	45	19.3ℓ	< 0.1ppb	#10 LD(A)	3.9ℓ	< 0.1ppb	0.8ppm	0.4ppm	95°F	26%	760mm	Fluorescent	50 fpm

BCME SAMPLING RESULTS

PLANT D PRODUCT TEXTILES

Sample Location	Sample #	Date of Sample	BCME Sample Tube #	Sample Volume	Result (PPB)	BCME Sample Derivative	Sample Volume	Result (PPB)	CH_2O Concentration	Cl^- Concentration	Temperature	Relative Humidity	Pressure	Lighting	Air Movement
Dryer (Frame) Entrance	28	1/28/76	27	42.6ℓ	(NIOSH)	#32 LD(A)	------	< 0.1ppb	0.9ppm	< 0.1ppm	85°F	18%	760mm	Fluorescent	<50fpm
Dryer (Frame) Entrance	38	1/30/76	4	17.6ℓ	N/A	#42 LD(A)	46.2ℓ	< 0.1ppb	0.3ppm	< 0.1ppm	81°F	23%	760mm	Fluorescent	70fpm
Dryer (Frame) Entrance	39	1/30/76	19	30.7ℓ	N/A	#10 LD(A)	40.1ℓ	< 0.1ppb	0.8ppm	< 0.1ppm	82°F	22%	760mm	Fluorescent	70fpm
Dryer (Frame) Entrance	40	1/30/76	11	37.9ℓ	N/A	#32 LD(A)	40.2ℓ	< 0.1ppb	0.3ppm	0.1ppm	90°F	12%	760mm	Fluorescent	100fpm
Dryer (Frame) Entrance	41	1/30/76	41	38.7ℓ	N/A	# 3 LD(B)	36.6ℓ	< 0.1ppb	0.6ppm	0.1ppm	84°F	17%	760mm	Fluorescent	65fpm
Dryer (Frame) Exit	28	1/28/76	27	26.0ℓ	(NIOSH)	#10 LD(A)	-------	< 0.1ppb	0.5ppm	0.1ppm	87°F	17%	760mm	Fluorescent	60fpm
Cure Oven Entrance	31	1/29/76	13	32.3ℓ	N/A	# 3 LD(A)	37.6ℓ	< 0.1ppb	<0.2ppm	0.2ppm	92°F	14%	760mm	Fluorescent	75fpm
Cure Oven Exit	30	1/29/76	28	19.3ℓ	N/A	#42 LD(A)	42.0ℓ	< 0.1ppb	<0.1ppm	0.2ppm	100°F	12%	760mm	Fluorescent	200fpm

BCME SAMPLING RESULTS

PLANT E PRODUCT TEXTILES

Sample Location	Sample #	Date of Sample	BCME Sample Tube #	Sample Volume	Result (PPB)	BCME Sample Derivative	Sample Volume	Result (PPB)	CH_2O Concentration	Cl^- Concentration	Temperature	Relative Humidity	Pressure	Lighting	Air Movement
Mixing Area	14	1/22/76	11	27.1ℓ	N/A	#10 LD(A) #10 LD(B)	8.5ℓ 10.2ℓ	<0.1ppb <0.1ppb	0.3ppm	0.3ppm	80°F	32%	760mm	Fluorescent	<50fpm
Mixing Area	17	1/22/76	41	29.7ℓ	N/A	#10 LD(C)	31.3ℓ	<0.1ppm	1.4ppm	0.2ppm	90°F	29%	760mm	Fluorescent	<50fpm
Pad Box	1	1/19/76	25 49	13.5ℓ 38.2ℓ	N/A N/A	---	----	------	0.3ppm	0.5ppm	77°F	26%	760mm	Fluorescent	<50fpm
Pad Box	4	1/20/76	26 15	39.3ℓ 10.7ℓ	N/A <0.1ppb	---	----	------	0.1ppm	<0.1ppm	84°F	32%	760mm	Fluorescent	<50fpm
Pad Box	5	1/20/76	21 38	42.9ℓ 31.1ℓ	N/A <0.1ppb	---	----	------	0.7ppm	<0.1ppm	91°F	70%	760mm	Fluorescent	<50fpm
Pad Box	7	1/20/76	--	----	----	# 3 LD(A)	10.0ℓ	<0.1ppb	-----	------	----	---	-----	----------	-----
Pad Box	8	1/20/76	--	----	----	#10 LD(A)	10.0ℓ	<0.1ppb	-----	------	----	---	-----	----------	-----
Pad Box	12	1/22/76	7	25.3ℓ	N/A	# 3 LD(A) # 3 LD(B)	12.7ℓ 10.0ℓ	<0.1ppb <0.1ppb	0.4ppm	0.1ppm	79°F	36%	760mm	Fluorescent	<50fpm
Pad Box	15	1/22/76	19	17.3ℓ	N/A	# 3 LD(C)	21.5ℓ	<0.1ppb	0.4ppm	0.3ppm	82°F	32%	760mm	Fluorescent	<50fpm
Pad Box	16	1/22/76	16	22.8ℓ	N/A	#32 LD(C)	36.3ℓ	<0.1ppb	0.5ppm	<0.1ppm	85°F	35%	760mm	Fluorescent	<50fpm

BCME SAMPLING RESULTS

PLANT E PRODUCT TEXTILES

Sample Location	Sample #	Date of Sample	BCME Sample Tube #	Sample Volume	Result (PPB)	BCME Sample Derivative	Sample Volume	Result (PPB)	CH_2O Concentration	Cl^- Concentration	Temperature	Relative Humidity	Pressure	Lighting	Air Movement
Pre Dryer Exit	6	1/20/76	7 14	40.5ℓ 34.4ℓ	N/A <0.1ppb	--------	-----	----	0.6ppm	0.1ppm	84°F	24%	760mm	Fluorescent	100fpm
Dryer (Frame) Entrance	2	1/19/76	8 29	34.5ℓ 34.2ℓ	N/A <0.1ppb	--------	-----	----	0.8ppm	0.3ppm	85°F	27%	760mm	Fluorescent	<50fpm
Dryer (Frame) Entrance	13	1/22/76	21	26.4ℓ	N/A	#32 LD(A) #32 LD(B)	13.6ℓ 11.3ℓ	<0.1ppm <0.1ppm	0.8ppm	0.1ppm	85°F	44%	760mm	Fluorescent	<50fpm
Dryer (Frame) Entrance	11	1/21/76	26	42.9ℓ	N/A	# 3 LD(A) # 3 LD(B)	2.1ℓ 5.0ℓ	<0.1ppb <0.1ppb	<0.1ppm	0.1ppm	83°F	56%	760mm	Fluorescent	<50fpm
Pre Calender	3	1/19/76	46 40	35.4ℓ 25.5ℓ	N/A <0.1ppb	--------	----	------	<0.1ppm	0.3ppm	73°F	18%	760mm	Fluorescent	150fpm
Cure Oven, Loop Dryer Entrance	9	1/21/76	8	41.5ℓ	N/A	#32 LD(A) #32 LD(B)	10.0ℓ 17.7ℓ	<0.1ppb <0.1ppb	0.2ppm	0.1ppm	92°F	23%	760mm	Fluorescent	50fpm
Cure Oven, Loop Dryer Exit	10	1/21/76	46	47.4ℓ	<0.1ppb	#10 LD(A) #10 LD(B)	7.7ℓ 15.3ℓ	<0.1ppb <0.1ppb	<0.1ppm	<0.1ppm	99°F	16%	760mm	Fluorescent	150fpm

BCME SAMPLING RESULTS

PLANT F _____ PRODUCT RESIN PAGE 1 of 1

Sample Location	Sample #	Date of Sample	BCME Sample Tube #	Sample Volume	Result (PPB)	BCME Sample Derivative	Sample Volume	Result (PPB)	CH_2O Concentration	Cl^- Concentration	Temperature	Relative Humidity	Pressure	Lighting	Air Movement
CH_2O, HCl Addition, Hood	91	4/5/76	-	-	-	-	-	-	<1.0 ppm	<1.0 ppm as HCl	73°F	-	760 mm	Fluorescent	142 fpm
"	96	4/6/76	-	-	-	-	-	-	"	"	"	69%	"	"	"
Oven Curing of Resin	92	4/5/76	#26	14.6ℓ	N/A	#22 LD(A)	6.8ℓ	<0.2 ppb	"	"	"	-	"	"	<50 fpm
"	93	"	-	-	-	#11 LD(A)	15.0ℓ	"	"	"	"	-	"	"	"
"	97	4/6/76	-	-	-	#0 LD(A)	15.3ℓ	"	-	-	"	69%	"	"	"
"	98	"	#35	22.8ℓ	N/A	#36 LD(A)	13.1ℓ	"	-	-	"	"	"	"	"
"	99	"	-	-	-	#42 LD(A)	15.2ℓ	-	-	-	"	"	"	"	"
Gel Treatment in Hood	94	4/5/76	#30	24.4ℓ	N/A	#18 LD(A)	13.7ℓ	<0.2 ppb	<1.0 ppm	<1.0 ppm as HCl	"	-	"	"	142 fpm
"	95	"	-	-	-	#22 LD(B)	11.3ℓ	"	"	"	"	-	"	"	"
" (Personne Sample)	100	4/6/76	-	-	-	#18 LD(B)	3.2ℓ	"	-	-	"	69%	"	"	"

N/A - not analyzed

BCME SAMPLING RESULTS

PLANT G PRODUCT FOUNDRY RESINS

Sample Location	Sample #	Date of Sample	BCME Sample Tube #	Sample Volume	Result (PPB)	BCME Sample Derivative	Sample Volume	Result (PPB)	CH_2O Concentration	Cl^- Concentration	Temperature	Relative Humidity	Pressure	Lighting	Air Movement
Hot Box Coremaking CR-158, C1580	101	5/4/76	#79	49.0ℓ	N/A	#3 LD(A)	18.2ℓ	<0.2 ppb	0.8 ppm	<1 ppm as HCl	73°F	25%	760 mm	Fluorescent	
"	102	"	#67	35.0ℓ	"	#42 LD(A)	16.2ℓ	"	0.9 ppm	"	"	"	"	"	<50 fpm
Hot Box Coremaking Cooling CR158,C1580	103	"	#72	21.0ℓ	"	#10 LD(A)	16.3ℓ	"	0.8 ppm	"	"	"	"	"	"
Hot Box Coremaking CR-105, C1050	104	"	#12	21.9ℓ	To KSC	#3 LD(B)	18.4ℓ	"	1.5 ppm	"	"	"	"	"	"
"	105	"	#3	36.5ℓ	N/A	#42 LD(B)	16.4ℓ	"	0.4 ppm	3.3 ppm as HCl	"	"	"	"	"
Hot Box Coremaking Cooling CR105,C1050	106	"	#53	"	"	#10 LD(B)	16.2ℓ	"	0.7 ppm	<1 ppm as HCl	"	"	"	"	""
Pouring CR158,C1580 (Stack)	107	5/5/76	#48	19.8ℓ	To KSC	#3 LD(A)	17.1ℓ	"	0.5 ppm	"	100°F +	-	"	"	"
" (Non-Stack)	108	"	#19	59.4ℓ	N/A	#10 LD(A)	15.6ℓ	"	<0.1 ppm	"	75°F	28%	"	"	"
Pouring CR105,C1050 (Non-stack)	109	"	#13	12.4ℓ	"	#42 LD(A)	38.0ℓ	"	"	"	"	30%	"	"	"
" (Stack)	110	"	#11	"	To KSC	#3 LD(B)	15.5ℓ	"	0.7 ppm	"	100°F +	-	"	"	"

BCME SAMPLING RESULTS

PLANT H PRODUCT FOUNDRY RESINS PAGE 1 of 1

Sample Location	Sample #	Date of Sample	BCME Sample Tube #	Sample Volume	Result (PPB)	BCME Sample Derivative	Sample Volume	Result (PPB)	CH_2O Concentration	Cl^- Concentration	Temperature	Relative Humidity	Pressure	Lighting	Air Movement
Shell Baking	111	8/4/76	#10	30.6ℓ	N/A	B-1	49.6ℓ	<0.2 ppb	< 1 ppm	< 1 ppm	89°F	36%	760 mm	Fluorescent	100 fpm
Shell Baking	112	"	#64	50.8ℓ	N/A	B-2	53.1ℓ	<0.2 ppb	< 1 ppm	< 1 ppm	84°F	26%	"	"	< 50 fpm
Shell Baking	113	"	#77	121.8ℓ	N/A	B-3	47.5ℓ	<0.2 ppb	< 1 ppm	< 1 ppm	79°F	46%	"	"	75 fpm
Shell Baking	114	"	#78	121.8ℓ	N/A	B-4	51.3ℓ	<0.2 ppb	< 1 ppm	< 1 ppm	80°F	46%	"	"	50 fpm
Pouring Area	115	"	#63	24.4ℓ	N/A	B-7	28.3ℓ	<0.2 ppb	4.5 ppm	< 1 ppm	87°F	31%	"	"	< 50 fpm
Pouring Area	116	"	#59	62.5ℓ	N/A	B-5	79.5ℓ	<0.2 ppb	< 1 ppm	< 1 ppm	-	-	"	"	"
Pouring Area	117	"	#69	12.6ℓ	N/A	B-6	31.9ℓ	<0.2 ppb	< 1 ppm	< 1 ppm	-	-	"	"	"
Pouring Area	118	8/5/76	#52	13.7ℓ	N/A	B-8	33.0ℓ	<0.2 ppb	5.5 ppm	< 1 ppm	-	-	"	"	"
Pouring Area	119	"	#62	33.0ℓ	N/A	B-9	35.7ℓ	<0.2 ppb	4.5 ppm	< 1 ppm	92°F	37%	"	"	"
Pouring Area	120	"	# 7	70.5ℓ	N/A	B-10	36.6ℓ	<0.2 ppb	< 1 ppm	< 1 ppm	93°F	38%	"	"	"

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