PROBLEM

As part of Dow's Product Stewardship Program, personnel in Designed Products TS&D, requested that the Industrial Hygiene Laboratory measure and evaluate the potential inhalation exposures to the residual monomers (vinylidene chloride and acrylonitrile) in soluble Saran resin manufactured by The Dow Chemical Company. The survey was completed at the Research and Development Laboratories of the Olin Corporation in Pisgah Forest, North Carolina, during the operation of packaging machines using Saran coated cellophane.

CONCLUSIONS

None of the 22 samples collected showed concentrations of vinyl chloride, vinylidene chloride, or acrylonitrile in excess of their current exposure criteria.

DISCUSSION

On August 15, 1974, a series of samples was collected at the Olin Corporation to measure airborne concentrations of vinyl chloride, vinylidene chloride and acrylonitrile. The samples were collected on activated charcoal using the apparatus shown in Figure 1. A portable battery powered pump was used to pass air at a constant flow rate through a tube containing activated charcoal adsorbent. Prior to the collection of each sample, a calibrated external rotameter was attached to the inlet side of the adsorber tube to measure

the air flow rate. This process was again repeated at the end of each sample collection interval, and the two readings were averaged in determining the air flow rate through the tubes. To enable calculation of the total volume of air sampled, the duration of each sample was also measured. In most instances, the samplers were positioned near the heat sealer bars or plates of packaging machines operating with Saran coated cellophane. The films used were types 160V587 and 250V5. Several samples were also collected at the breathing zone of the laboratory technician who was operating the packaging equipment. Later in the survey, this same sampling equipment was transported to the production area where samples were collected at breathing zone area locations near "A" tower (where the Saran resin was being applied to the cellophane) and also at the mix tank (where the resin was dissolved in solvent).

In the R&D Laboratory, four impinger samples were collected using the apparatus shown in Figure 2. A pump was used to draw air, at approximately 20 liters per minute, through a large impinger. Hydrogen chloride in the inlet air was absorbed in the distilled water contained in the impingers.

All samples were returned to Midland, Michigan, where they were submitted to the Dow Analytical Laboratory for analysis.

The charcoal adsorbent samples were extracted with carbon disulfide, and the extracts were subsequently analyzed by gas chromatography using flame ionization detection. The results were compared with the volumes of air sampled in order to calculate airborne concentrations in ppm (parts per million, volume/volume). These results are listed in Table 1. The aqueous solutions from the impingers were analyzed for chloride using the specific ion electrode. As with the adsorbent samples, the results were compared with the air volumes sampled to obtain the concentration values appearing in Table 2.

To be more meaningful, the observed vapor concentrations need to be compared with exposure criteria. The appropriate criteria for the compounds encountered during this survey are as follows:

Compound	Type	Limit, ppm	Source
Vinyl chloride	TWA	1	OSHA
Vinyl chloride	EL	5	OSHA
Vinylidene chloride	TWA	10	ACGIH
Vinylidene chloride	EL	20	ACGIH

Compound	Type	Limit, ppm	Source
Acrylonitrile	TWA	20	OSHA
Acrylonitrile	EL	30	ACGIH
Toluene	TWA	200	OSHA
Toluene	TWA	100	ACGIH
Toluene	EL	150	ACGIH
Tetrahydrofuran	TWA	200	OSHA
Tetrahydrofuran	EL	250	ACGIH
Hydrogen chloride	C	5	OSHA

where, TWA = Time-Weighted Average

EL = Excursion Limit

OSHA = Occupational Safety and Health Administration

ACGIH = American Conference of Governmental Industrial Hygienists

C = Ceiling

Exposure criteria refer to airborne concentrations of substances and represent conditions under which it is believed that nearly all workers may be repeatedly exposed day after day throughout a working life time without adverse effects. TWA values refer to time-weighted average concentrations for an eight-hour work day and a forty-hour work week. Because TWA exposures are averages over an eight-hour day, exposures are permitted at concentrations in excess of the TWA exposure criteria. In a hypothetical situation, however,

an employee could be exposed to a very high concentration of a material for a short period of time such that some ill effects (such as headache, nausea, irritation, etc.) were encountered, yet the eight-hour TWA exposure was within the allowable limit. To prevent exposures such as these from being classified as "acceptable," the ACGIH has recommended a set of excursion factors used in calculating excursion limits. Exposures in excess of the excursion limits should be avoided in the interest of the health and comfort of employees.

There are some materials which are predominatly fast acting (in a detrimental manner) and whose exposure criteria are based on this particular response. These types of substances are best controlled in the working environment by a ceiling limit above which no exposures should be allowed. The 5 ppm ceiling concentration assigned for hydrogen chloride was established because of its severe irritative properties at concentrations exceeding that level.

In a comprehensive industrial hygiene survey to determine personnel inhalation exposures, numerous samples would be collected for varying times to determine the workers' eight-hour TWA exposures. Short term samples would also be collected to permit determination of transient exposures encountered

during the work day at specific work areas or operations. This survey was an attempt to simulate exposure levels which could be encountered in packaging operations utilizing Saran coated cellophane. Since the survey was carried out in the R&D laboratory, it was not a "steady-state" operation so sampling times were limited. Many of the samples were collected in close proximity to the source of the potential air contaminant to determine maximum vapor concentrations. At the sealing operations, this source was the heat sealer bars or plates. Table 1 shows that the levels of vinyl chloride, vinylidene chloride and acrylonitrile were well within the exposure criteria currently defined for these materials. Some THF (tetrahydrofuran) and toluene concentrations are also listed in Table 1. Sample 20 was collected in a breathing zone area location on the south side of the coater roll of "A" tower and showed a high concentration of THF. Samples 19 and 20 were both collected near the base of "A" tower and may not represent actual breathing zone locations. These samples were collected primarily to determine the residual monomer (vinyl chloride, vinylidene chloride and acrylonitrile) concentrations at these particular work areas. If THF and toluene exposures of tower operators need to be determined, a more comprehensive survey would obviously be required.

The hydrogen chloride concentrations measured near the heat

sealer of the Oliver packaging machine were within the 5.0 ppm ceiling concentration for HCl. It may therfore be assumed that exposures of people operating such a machine would be even lower at their breathing zones. This was not the situation found with the samples taken near the Doboy packaging machine. While 49 and 69 ppm levels were definitely in excess of the 5 ppm standard, it is important to emphasize that both samples taken at the Doboy machine were collected inside the enclosure housing the rotary end-sealing bars. This enclosure acts as a trap to contain the fumes and vapors generated in the heat sealing process. No impinger samples were collected at the breathing zone of the Doboy machine operator to determine hydrogen chloride exposure, however, plans include future measurement and evaluation of those exposures to HCl.

Figure 1. APPARATUS USED FOR SAMPLING AIR FOR SARAN MONOMERS AT THE OLIN CORPORATION, AUGUST 15, 1974

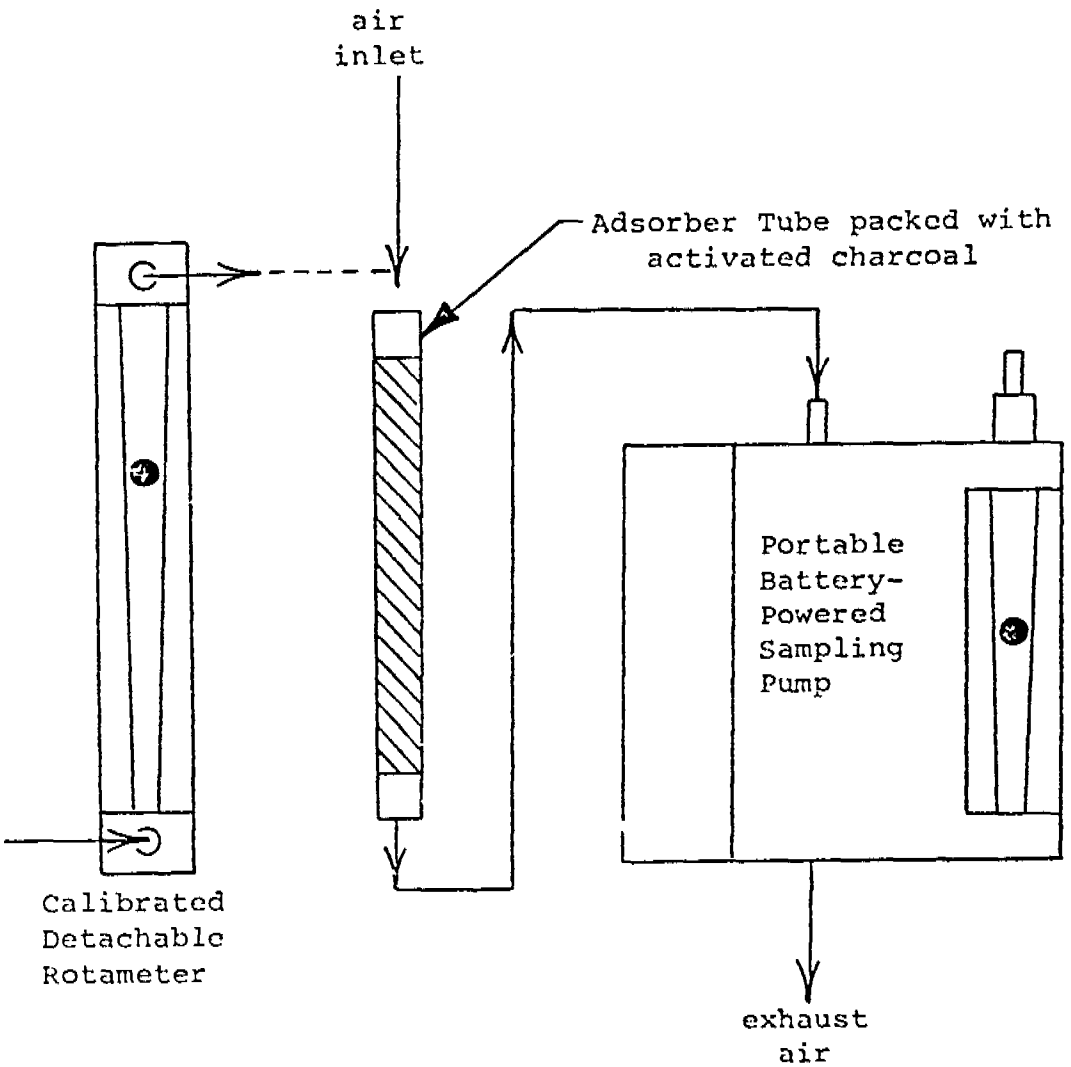

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Figure 2. APPARATUS USED FOR SAMPLING WATER SOLUBLE CHLORIDES (AS HYDROGEN CHLORIDE) IN AIR AT THE OLIN CORPORATION, AUGUST 15, 1974

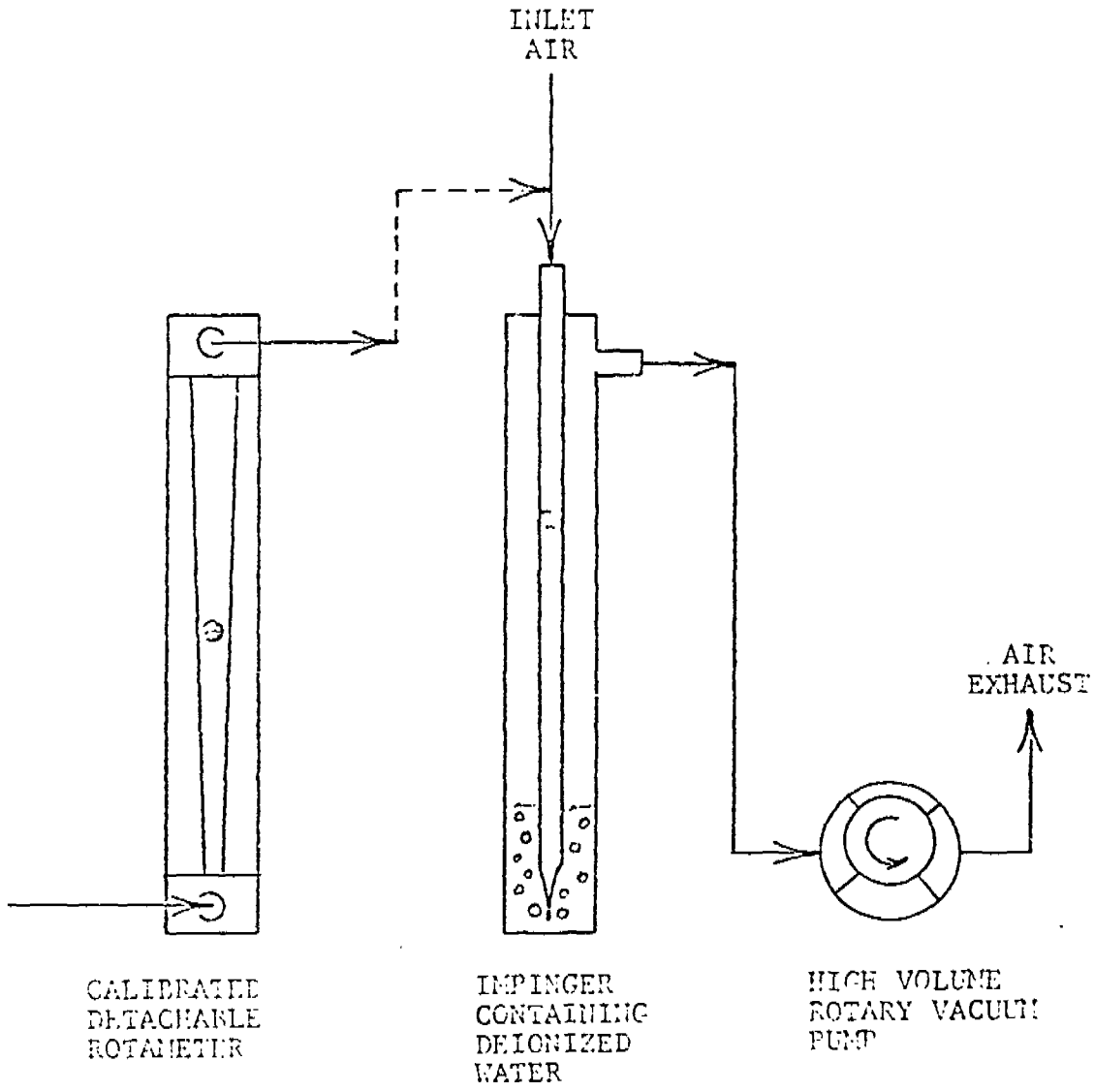

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Table 1. RESULTS OF ADSORBER SAMPLES COLLECTED DURING THE HEAT SEALING OF SARAN COATED CELLOPHANE AT THE OLIN CORPORATION, PISGAH FOREST, NORTH CAROLINA AUGUST 15, 1974

Sample Description	Spl. No.	Film Type	Concentration, Parts Per Million: Vinyl Chloride	Vinylidene Chloride	Tetra-hydro-furan	Toluene	Acrylo-nitrile
Five inches above rotary sealer bars of the Doboy packager. Source samples, not breathing zone; 500°F sealer temperature.	1	160V587	0.05	0.20	1.6	1.0	NA*
	2	160V587	0.05	0.28	1.6	1.0	NA
	5	250V5	0.04	0.24	0.28	0.49	0.09
	6	250V5	0.03	0.13	0.20	0.42	<0.08
Breathing zone (personal monitor sample) of Doboy packager operator.	3	160V587	0.03	<0.01	NA	NA	<0.08
	7	250V5	0.02	<0.01	NA	NA	<0.08
Breathing zone at the control panel of the Doboy packager.	4	160V587	0.02	<0.01	NA	NA	<0.08
	8	250V5	0.02	<0.01	NA	NA	<0.08
Source sample (not breathing zone) on package pusher rod of Oliver packager. Approx. 375°F sealer temperature	9	160V587	0.01	<0.01	0.5	0.4	<0.08
	10	160V587	0.01	<0.01	NA	NA	<0.08
	15	250V5	0.04	<0.01	NA	NA	<0.08
	16	250V5	0.01	<0.01	NA	NA	<0.07
Breathing zone (personal monitor sample) of Oliver packager operator.	11	160V587	0.02	<0.01	NA	NA	<0.08
	17	250V5	0.01	<0.01	NA	NA	<0.08
Breathing zone area at box feeding/product receiving station of Oliver packager.	12	160V587	0.02	<0.01	NA	NA	<0.08
	18	250V5	0.01	<0.01	NA	NA	<0.08

* No Analysis

Table 1. CONTINUED

Sample Description	Spl. No.	Film Type	Concentration, Parts Per Million: Vinyl Chloride	Vinylidene Chloride	Tetra-hydro-furan	Toluene	Acrylo-nitrile
Source sample one inch above film being drawn across a heated (500°F) bar (at slitter).	13	250V5	0.03	<0.01	1.0	2.7	<0.2
	14	250V5	0.03	0.04	2.0	5.7	<0.2
Breathing zone area on the north side of the coater roller of "A" tower.	19	--	0.01	0.01	150.0	6.6	NA
Breathing zone area on the south side of the coater roller of "A" tower.	20	--	0.01	0.06	610.0	46.0	NA
Breathing zone area above open manhole of mix tank where XD-7651.1 resin was unloaded from 1100 pound cartons.	21	--	0.01	<0.01	22.0	3.9	NA
	22	--	0.01	0.01	21.0	4.0	NA
TIME-WEIGHTED EXPOSURE CRITERION			1.0**	10.0***	200.0**	200.0**/ 100.0***	20.0**
EXCURSION EXPOSURE CRITERION			5.0**	20.0***	250.0***	150.0***	30.0***

*No Analysis
**OSHA (Occupational Safety & Health Act)
***ACGIH (American Conference of Governmental Industrial Hygienists)

Table 2. RESULTS OF IMPINGER SAMPLES COLLECTED DURING THE HEAT SEALING OF SARAN COATED 160V587 CELLOPHANE AT THE OLIN CORPORATION, PISGAH FOREST, NORTH CAROLINA, AUGUST 15, 1974

Sample No.	Sample Location	HCl conc., ppm
1	Five inches above rotary heat sealer bars of the Doboy packaging machine. Source sample; not breathing zone.	49.0
2	Five inches above rotary heat sealer bars of the Doboy packaging machine. Source sample; not breathing zone.	49.0
3	Near the heat sealer of the Oliver packaging machine. Source sample; not breathing zone.	3.9
4	Near the heat sealer of the Oliver packaging machine. Source sample; not breathing zone.	0.31

NOTE: ABOVE DATA BASED ON 79% RECOVERY