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HAZARD EVALUATION AND TECHNICAL ASSISTANCE REPORT
HETA 88-010-L1982
NEVILLE CHEMICAL COMPANY
ANAHEIM, CALIFORNIA
AUGUST 1989

Hazard Evaluations and Technical Assistance Branch
Division of Surveillance, Hazard Evaluations and Field Studies
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I. INTRODUCTION

On October 7, 1987, a representative of the Oil Chemical and Atomic Workers International Union (OCAW) requested that NIOSH conduct a Health Hazard Evaluation at the Neville Chemical Company, Anaheim, California. The requestor was concerned with the recent death of one employee from what was believed to be liver cancer, and a second employee who was thought to have an "abnormal liver." A concern was expressed with exposures during the carbon resin manufacturing process carried out at the plant.

In response to this request, a combined medical-environmental site visit was conducted at the Neville Chemical Company facility on November 18th and 19th, 1987. An opening conference was held with management and union representatives during which the basis for the request was discussed along with the nature of the plant operations. Following this meeting, a walk-through inspection of the facility was conducted. During the course of the survey, confidential interviews were conducted with eleven employees who worked at the plant. Material safety data sheets were reviewed, and environmental samples were collected to determine concentrations of identifiable airborne organic substances. On December 17, 1987, a follow-up environmental survey was conducted to assess particulate exposures during the carbon resin bagging operation.

II. BACKGROUND

The plant, which began operations in 1958, manufactures petroleum resins (thermoplastic polymers with an average molecular weight less than 2000) by polymerizing organic molecules five to twelve carbon atoms in size. The production processes have remained relatively unchanged since the opening of the plant in 1958; however, in recent years because of a fall-off in demand for their products, the amount of resins produced has fallen to about one-half of the plant capacity.

The plant uses both a catalytic and a thermal polymerization process to produce the hydrocarbon resins. The raw materials for the process consist of cracked petroleum fractions, which contain a wide variety of aliphatic and aromatic hydrocarbons. The raw materials are brought into the plant by rail car and then pumped to storage tanks. In the

catalytic process, the resin components are first blended and subsequently injected with boron trifluoride (BF_3) in a pre-reactor. The mixture is then cooled in a secondary reactor where it forms a "polyoil". After aging in a batch tank, the polyoil is pumped through packed clay towers to neutralize the excess BF_3 and decolorize the liquid. The finished polyoil is kept in storage tanks until it is pumped to distillation towers where the remaining light solvent oil fraction is removed. The resin is then pumped to an accumulator where it is stored until final use. The resin can then be diluted with an oil for shipment from the plant as a liquid, or can be flaked and packaged for shipment as a solid resin.

The flaking and packaging operation is conducted in a warehouse located adjacent to the accumulators. Two employees are responsible for the packaging operations, and rotate bag filling every one-half hour. The bagging operation is equipped with local exhaust ventilation. In addition, both employees wear disposable dust masks (TC 21C 271) during the bagging operation.

The thermal polymerization process takes place in a manner similar to the catalytic process except that different proportions of the starting raw materials are used. In addition, instead of using the BF_3 catalyst, heat and pressure are used to carry out the polymerization reaction.

While most of the hydrocarbon resin is produced from the cracked petroleum fractions, on occasion (reportedly < 5% of the time), coumarone - indene or coal-tar resins are produced. This process is similar except that a portion of the starting raw materials may be coal-tar derivatives instead of petroleum derivatives.

At the time of the survey, there were 16 hourly production employees who worked on the plant's three shifts. These included two laboratory workers, three plant operators, four treaters, three helpers, three maintenance employees, and one packager.

The employees undergo a pre-employment physical, but no periodic medical examinations are conducted. The employee turn-over is low and the employees working at the plant have an average of about 10 years of seniority.

A previous health hazard evaluation had been conducted at a similar operation at the company's facility near Pittsburgh, Pennsylvania in 1976. During this survey, concentrations of respirable dust in the packaging area were found to exceed the environmental evaluation criteria.[1] No over-exposure to any organic solvents was found during the 1976 survey.

III. MATERIALS AND METHODS

A. Medical

During the initial survey on December 18 and 19, 1979, confidential medical interviews were conducted with the employees present at the plant during the day and evening work shifts. One employee, who was absent from work because of illness, was interviewed at his residence. Material safety data sheets for the materials used in the production process were also reviewed.

B. Environmental

On November 18 and 19, 1987, an environmental survey was conducted at Neville Chemical Company to assess employee exposures to the various airborne hydrocarbons that might be present because of their use as raw materials or their presence as intermediate products in the production process. During this survey, personal breathing zone (PBZ) air samples were collected near the breathing zone of each of the workers present on the day shift at the plant. Samples were obtained using battery-powered pumps operating at 50 and 200 cubic centimeters (cc) of air per minute. The pumps were attached by Tygon tubing to the charcoal tube collection medium. Two of the charcoal tubes with the higher sample volumes were screened by mass spectrophotometry, and their components qualitatively identified. The remaining samples were then quantified for identifiable substances.

On December 17, 1987, a follow-up environmental survey was conducted to assess exposures in the flaker/packaging operations which were not operating during the initial survey. During this survey, personal breathing zone and general area air samples were collected for total and respirable particulate. (The vast majority of particulate would be expected to consist of dried hydrocarbon resin.) Samples were obtained using battery-powered sampling pumps operating at 1.7 liters of air per minute. The pumps were attached by Tygon tubing to the collection medium of pre-weighed polyvinyl chloride (PVC) filters contained in 2-piece plastic cassettes. In addition, a ten-millimeter nylon cyclone was used to collect the respirable dust samples. The filters were replaced approximately halfway through the work shift. The samples were analyzed for total weight using NIOSH Method 7300.[2]

IV. EVALUATION CRITERIA

A. Environmental

As a guide to the evaluation of the hazards posed by workplace exposures, NIOSH field staff employ environmental evaluation criteria for assessment of many chemical and physical agents.

These criteria are intended to suggest levels of exposure to which most workers may be exposed up to 10 hours per day, 40 hours per week, for a working lifetime, without experiencing adverse health effects. It is important, however, to note that not all workers will be protected from adverse health effects if their exposures are maintained below these levels. A small percentage may experience adverse health effects because of individual susceptibility, a preexisting medical condition, and/or a hypersensitivity (allergy).

In addition, some hazardous substances may act in combination with other workplace exposures, the general environment, or with medications or personal habits of the worker to produce health effects even if the occupational exposures are controlled at the level set by the evaluation criterion. These combined effects often are not considered in the evaluation criteria. Also, some substances are absorbed by direct contact with the skin and mucous membranes and, thus, potentially increase the total exposure. Finally, evaluation criteria may change over the years as new information on the toxic effects of an agent becomes available.

The primary sources of environmental evaluation criteria for the workplace are: (1) NIOSH Criteria Documents and recommendations, (2) the American Conference of Governmental Industrial Hygienists' (ACGIH) Threshold Limit Values (TLVs), (3) the U.S. Department of Labor/Occupational Safety and Health Administration (OSHA) occupational health standards [Permissible Exposure Limits (PEL's)]. Often, the NIOSH recommendations and ACGIH TLV's are lower than the corresponding OSHA standards. Both NIOSH recommendations and ACGIH TLVs usually are based on more recent information than are the OSHA standards. In evaluating the exposure levels and the recommendations for reducing these levels found in this report, it should be noted that the company is required by the Occupational Safety and Health Administration to meet those levels specified in an OSHA standard.

A time-weighted average (TWA) exposure refers to the average airborne concentration of a substance during a normal 8- to 10-hour workday. TWA's for the major contaminants evaluated during this survey are presented at the end of Tables 1 through 3.

Simultaneous exposure to substances, such as solvents, which affect the body in a similar fashion may have an additive effect. To evaluate these additive effects, the exposure level of each substance is computed as a percentage of the evaluation criterion for that substance. If the sum of these percentages exceeds 100%, the worker is considered to be over-exposed to that mixture of substances.

B. Toxicology

There is little toxicology data concerning the health effects of petroleum resins like those produced at Neville. However, because of the relatively high molecular weight of the resin (2000), these resins are likely to be of low toxicity.

The raw materials used during the production of the hydrocarbon resin consisted primarily of cracked petroleum derivatives. These materials ranged from five to twelve carbons in size and included a wide variety of aliphatic and aromatic hydrocarbon solvents. In lieu of a detailed discussion of the individual toxicity of each of the components, a general discussion of petroleum solvent toxicity is presented below.

Petroleum solvents may cause irritation of the eyes, nose and throat. Effects of direct skin contact with solvents range from dry skin or mild rash to a dry, scaly, fissured dermatitis. High air concentrations of these chemicals affect the central nervous system (CNS) such that exposed workers may complain of headache, nausea, lightheadedness, dizziness, and incoordination. High exposure to these compounds can adversely affect the liver and kidney. One particular organic solvent, benzene, has been shown to cause cancer in humans.

Recent research on the effects of exposure to low levels of solvent mixtures has focused on behavioral and psychological effects which may show nervous system damage or deviations from normal CNS function.[3] For example, an epidemiology study was conducted on Finnish car painters exposed to a mixture of toluene, xylene, butyl acetate, and white spirits for a mean duration of 15 years. Average combined exposures were less than 32% of ACGIH TLV's, however, researchers found more memory disturbances, decreased vigilance, and more absent-mindedness among car painters when matched with railroad engineers as controls. Visual intelligence and verbal memory were the most affected. The authors concluded that car painters, although not ill in the clinical sense, showed clear signs of central and peripheral nervous system lesions more often than members of the control group.[4,5]

V. RESULTS AND DISCUSSION

A. Medical

A review of the death certificate and company records and of the deceased employee who was thought to have died from liver cancer indicates that the employee succumbed at age 43 to a tumor of the stomach which metastasized to the liver. A review of the medical records of the employee who was thought to have an "abnormal liver" revealed that this liver abnormality was due to an infectious process. In addition, it was later reported that another long term employee (14 years) succumbed to pancreatic cancer in 1988.

Interviews with the remaining workers revealed that the employees ranged in age from 29 to 60 (mean age 42) and had worked at the plant for 1 1/2 years to 23 years (mean length of service 9.4 years). The present health of the majority of the workers was reported as excellent; however, one worker reported having severe back problems, one worker reported having had a cerebral vascular accident and a myocardial infarction, and, as mentioned above, one patient had experienced an infection in his liver.

With regard to working conditions at the Neville facility, the majority of the employees reported three major areas of concern. The first was the periodic cleaning of the clay filter towers. Reportedly approximately one to two towers per month must be cleaned by a team of two men. The final process in this cleaning requires entry of one of the employees into the tower to remove the last portions of clay and gravel. On occasion, there reportedly was a strong chemical odor present in the tanks, even after a lengthy period of steam cleaning. The workers reported that an air-supplied respirator has been available for use within the cleaning tower for about 10 years, but that on occasion this mask was difficult to use because it impaired the worker's vision. (Management reported that an improved method of cleaning the clay towers that would not require the employees to enter the tower was under development.)

Four workers mentioned concern about exposure to boron trifluoride while working in the treater facility. Under normal operations the boron trifluoride is in an enclosed system. On occasion, employees reported that leaks of the boron trifluoride developed either while transferring this chemical during the production process or when replenishing the boron trifluoride reservoir from a transport trailer. During these episodic leaks the workers reported that they would have to enter the contaminated area to tighten the valves or stop the leak. The workers reported that recently a half-face piece airline respirator had been installed at the treater site. However, when the workers entered the boron trifluoride clouds they still did so without using goggles to protect their eyes from the irritating boron trifluoride fumes.

Three workers also reported that resin dust exposures encountered while working as a packager in the warehouse were, on occasion, very severe, especially when the dust removal ventilation was inoperative. It is of note that one worker, who frequently worked in packaging, was experiencing a chronic perforation of the nasal septum, a condition that can be exacerbated by high dust exposure.

B. Environmental

Two of the air samples collected on the plant personnel were used to help in the qualitative identification of the organic substances present in the plant environment. The chromatograms for these

samples, showing the identifiable substances, are presented in Diagrams 1 & 2. Table 1 shows the results of the remaining samples which were quantified for specific organic compounds. The major compounds found to be present were the organic solvents toluene, xylene, styrene, and dicyclopentadiene (DCPD). The remaining hydrocarbons were quantified and expressed as an airborne concentration of "total other hydrocarbons." As evidenced by the results shown in this table, the concentrations of each of these substances were far below their respective environmental criteria. When the formula for the additive effects of exposures is applied, the results are also below the combined evaluation criterion.

Tables 2 and 3 show the results of the environmental samples collected during the resin bagging procedure. As evidenced by these data, TWA concentrations of 1.6 and 4.0 milligrams per cubic meter of air (mg/M^3) total particulate were found in the two PBZ samples collected for the packaging employees. These concentrations were below the ACGIH TLV of 10 mg/M^3 for nuisance particulate. It should be noted that both of the employees were wearing respirators, and if properly fitted and maintained, their actual exposures would have been substantially lower. Concentrations of total particulate in area samples collected around the packaging area ranged from 1.0 to 2.0 mg/M^3. Concentrations of 0.3 and 0.4 mg/M^3 respirable particulate were found in two area samples collected near the packaging operation which were below the ACGIH TLV of 5 mg/M^3. It should be noted that the employees rotated one half hour on and one half hour off on the packaging operation. Had one employee worked this operation for the entire shift, his dust exposure would have been considerably higher.

VI. CONCLUSIONS AND RECOMMENDATIONS

In regard to the requestor's concern with 2 employees believed to have liver disease, it appears that the first employee had stomach cancer rather than liver cancer, and that the abnormality in the liver of the second employee was due to an infectious process not related to employment at the facility.

The environmental data collected during this evaluation did not reveal any airborne exposures above the evaluation criteria. Since the resin production process takes place in an enclosed system of pipes, reactor vessels and stills, any exposures which take place during the actual production operations would most likely result from "fugitive emissions." These emissions are generally the result of leaks in valves, pumps, flanges, and other pieces of equipment in the process stream. Since volatile components of the process stream can escape in this manner, it is important to use regular leak detection and repair programs and state-of-the- art control techniques to reduce these emissions as much as possible. Several sources of information which deal with these emissions and their control are available and should be consulted for more detailed information.[6,7]

Maintenance activities, both routine and non-routine, present another area where higher employee exposures could be encountered. Any work done on process equipment where residual hydrocarbon liquid or vapor may be present can pose a much greater potential exposure hazard to the employees. Therefore, it is essential that the appropriate skin and respiratory protection equipment be provided based on an assessment of the degree of hazard involved. Maintenance work which involves entry into confined spaces, such as the cleaning procedures used for the clay towers, deserve strict attention because of the many related health and safety hazards which can exist in these operations. Strict procedures for confined space entry, such as those contained in the NIOSH Criteria for a Recommended Standard...Working in Confined Spaces, (a copy of which was provided to the employer), should be adopted for these situations.[8] Supervisory oversight should be carried out to ensure that these procedures are routinely followed.

Leaks and spills are another potential source of employee exposure to high contaminant concentrations. One example cited during the employee interviews were occasions on which boron trifluoride leaks reportedly occurred in the treater area. In order to prevent such occurrences, process components which contain or transport these materials should be regularly inspected for their integrity, particularly in circumstances where substances of high acute toxicity, such as boron trifluoride, are present. In addition, contingency plans which detail specific emergency procedures, including the selection of the appropriate protective clothing and respiratory protection, should be in place to help respond to any spills or leaks which might occur.

Because of their inherent limitations, respirators should not be considered a primary means of employee protection. However, the use of respiratory protection is a suitable means of exposure control in the event that engineering controls cannot feasibly reduce the exposure levels, such as during non-routine maintenance activities and emergencies. In order to ensure the effective use and function of the respirators, a comprehensive respiratory protection plan should be put in place. Such a program is outlined by the American National Standard Institute in the ANSI Standard Z88.6-1984.[9] The program should include a written standard operating procedure which addresses respirator selection, training, fitting, testing, inspection, cleaning, maintenance, storage, and medical examinations. A detailed discussion of these key program elements is contained in the NIOSH Guide to Industrial Respiratory Protection, a copy of which has been provided to the employer.[10]

While exposures during the resin packaging procedure were below the evaluation criteria for nuisance dust, it is not clear that this standard is appropriate for the resin dust. No reports could be located concerning the possible toxicity of petroleum resins, but the lack of studies does not necessarily assure safety. Given the paucity of toxicological data, it would be advisable to make further

improvements in the ventilation system to reduce these resin exposures which could approach the recommended nuisance dust limit for a worker who spent a full work shift packaging resins. Several recent studies have documented improved dust control systems for bag-filling machines which have greatly reduced exposures in the applications examined. More detailed information, including engineering drawings of various types of these dust control systems, are available from the U.S. Bureau of Mines.[11]

VII. REFERENCES

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10. National Institute for Occupational Safety and Health. Guide to Industrial Respiratory Protection. Cincinnati, Ohio. National Institute for Occupational Safety and Health, 1987. (DHHS (NIOSH) Publication No. 87-116).

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TABLE 1

Results of Personal Breathing Zone Air Samples Collected for Organic Vapors
Neville Chemical Company, Anaheim, California
November 19, 1987

Job Title	Work Location	Sample Time (minutes)	Sample Volume (liters)	Time-Weighted Average Concentrations Toluene (mg/M3)	Xylene (mg/M3)	Styrene (mg/M3)	DCPD (mg/M3)	Other Hydrocarbons (mg/M3)
Maintenance	Resin Tower	249	54.8	Sample Used in Qualitative Analysis - See Attachment 1				
Maintenance	Resin Tower	249	14.7	4.47	0.54	< LOD	< LOD	< LOD
Maintenance	Repair Shop	248	56.2	11.6	2.03	trace*	0.21	5.18
Maintenance	Repair Shop	248	53.5	9.18	1.59	< LOD	0.50	6.77
Maintenance	Plant-Wide	246	51.6	1.9	1.22	< LOD	trace*	2.42
Maintenance	Plant-Wide	246	27.3	1.9	1.22	< LOD	trace*	trace*
Operator	Control Room	246	52.8	Sample Used in Qualitative Analysis - See Attachment 2				
Operator	Control Room	246	13.8	trace*	0.24	< LOD	< LOD	(2.23)*
Helper	Plant-Wide	235	50.6	0.07	0.26	0.26	trace*	6.26
Helper	Plant-Wide	235	12.2	trace*	trace*	< LOD	< LOD	trace*
Evaluation Criteria								
NIOSH Recommended Exposure Limit (8-hour TWA)				375	434	213**	NA	350***
OSHA Permissible Exposure Limit (8-hour TWA)				375	435	215**	30	525***
ACGIH Threshold Limit Value (8-hour TWA)				375	435	215**	30	525***

Abbreviations and Key

DCPD - Dicyclopentadiene
mg/M^3 - milligrams of contaminant per cubic meter of air
< LOD - Less than the limit of detection of 3 micrograms for styrene and dicyclopentadiene and 20 micrograms for total hydrocarbons
* - less than the limit of quantitation: But greater than the limit of detection
** - Skin absorption can also contribute to the overall exposure
*** - The criteria for stoddard solvent is used for the "other total hydrocarbons".

TABLE 2

RESULTS OF SAMPLES COLLECTED FOR TOTAL PARTICULATE DURING RESIN PACKAGING
Neville Chemical Company, Anaheim, California
December 17, 1987

SAMPLE TYPE	SAMPLE DESCRIPTION	MINUTES SAMPLED	LITERS SAMPLED	TWA CONCENTRATION TOTAL PARTICULATE (mg/M3)
Personal	Packager #1 (am)	248	422	1.5
	Packager #1 (pm)	143	243	1.8
		391	Cumulative TWA	1.6
Personal	Packager #2 (am)	242	411	3.4
	Packager #2 (pm)	144	245	5.1
		386	Cumulative TWA	4.0
Area	5' to Left of Packager (am)	232	394	1.2
	5' to Left of Packager (pm)	152	258	0.6
		384	Cumulative TWA	1.0
Area	2' to Right of Packager (am)	212	360	2.3
	2' to Right of Packager (pm)	160	272	2.0
		372	Cumulative TWA	
Area	BZ Height at Work Station (am)	212	360	1.7
	BZ Height at Work Station (pm)	156	265	2.0
		368	Cumulative TWA	1.8
Area	Middle of Warehouse (am)	213	362	1.0
	Middle of Warehouse (pm)	148	252	1.0
		361	Cumulative TWA	1.0

Evaluation Criteria -Nuisance Dust - Total Particulate
ACGIH TLV - 10 mg/M^3, 8-hour TWA
OSHA PEL - 15 mg/M^3, 8-hour TWA

Abbreviations and Key
TWA - Time-weighted average
mg/M^3 - milligrams per cubic meter of air

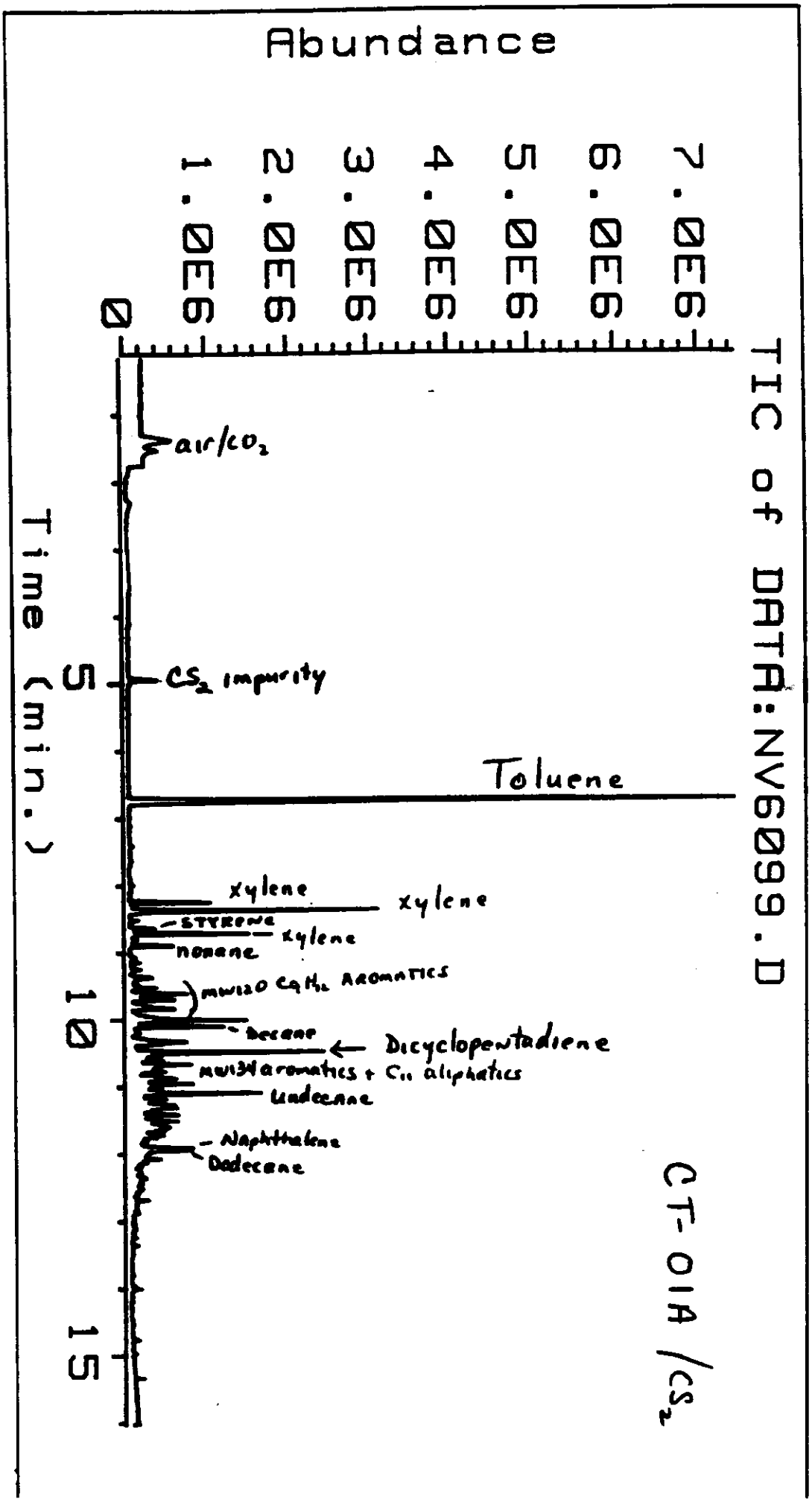
TABLE 3

RESULTS OF SAMPLES COLLECTED FOR RESPIRABLE PARTICULATE
DURING RESIN PACKAGING
Neville Chemical Company, Anaheim, California
December 17, 1987

SAMPLE TYPE	SAMPLE DESCRIPTION	MINUTES SAMPLED	LITERS SAMPLED	TWA CONCENTRATION TOTAL PARTICULATE (mg/M3)
Area	5' to Left of Packager (am)	232	394	0.2
	5' to Left of Packager (pm)	152	258	0.4
		384	Cumulative TWA	0.3
Area	2' to Right of Packager (am)	212	360	0.4
	2' to Right of Packager (pm)	160	272	0.4
		372	Cumulative TWA	0.4

Evaluation Criteria -Nuisance Dust - Respirable Fraction
OSHA PEL - 5 mg/M^3, 8-hour TWA

Abbreviations and Key
TWA - Time-weighted average
mg/M^3 - milligrams per cubic meter of air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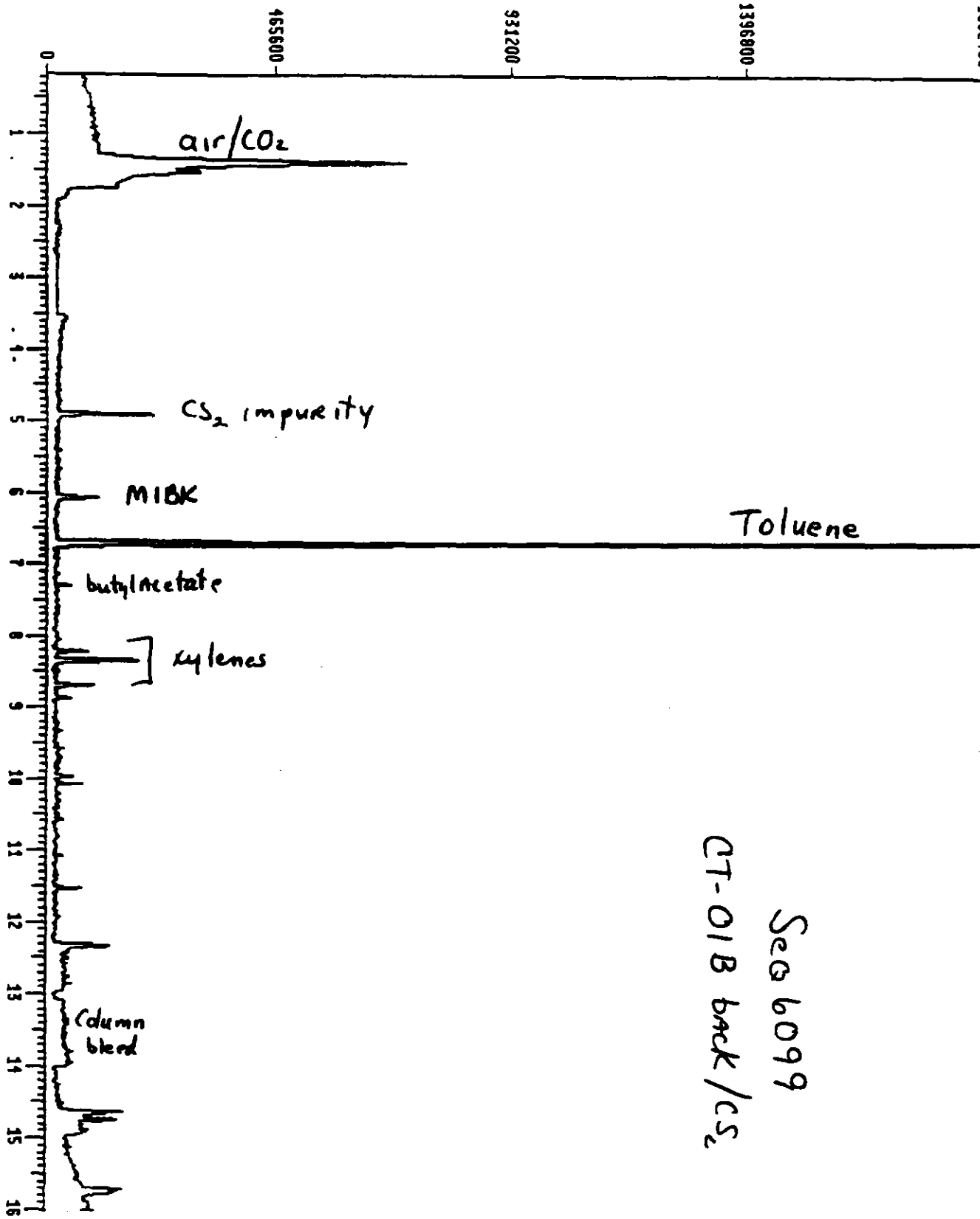

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