FLUOROCARBONS

INDUSTRIAL HYGIENE SURVEY REPORT

Allied Chemical
Danville, Illinois

Survey Dates: March 30-31, 1976
August 23-24, 1977

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Worker exposures to trichlorofluoromethane (75694) (G11), dichlorofluoromethane (75434) (G12) and carbon-tetrachloride (56235) (CC14) were surveyed at Allied Chemical (SIC-2869), Specialty Chemical Division, in Danville, Illinois, on March 30 and 31, 1976, and August 23 and 24, 1977. The company employed 44 to 74 workers, and provided medical and industrial hygiene services. In the product manufacturing area, personal exposures to G11, G12 and CC14 ranged from 3.5 to 39.3, 0.2 to 43.1, and 0.17 to 1.9 parts per million (ppm), respectively. In the product packaging areas, G11 and G12 concentrations ranged from 6.2 to 764.0 and 0.5 to 73.0ppm, respectively; no CC14 was detected. Current exposure standards are 5600 milligrams per cubic meter (mg/cu m) for G11, 4950mg/cu m for G12, and 720mg/cu m for CC14. The author recommends continued use of existing engineering controls, better use of enclosures in the packaging area, and use of dry ice to chill sample cylinders.

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NIOSH Project Officer: Jim Oser

Tracor Jitco Project Director: George R. Pielmeier

ABSTRACT

This industrial hygiene survey at Allied Chemical, Specialty Chemicals Division, Danville, Illinois, was specifically concerned with evaluating two fluorocarbons (GENETRON®), trichlorofluoromethane (G11) and dichlorodifluoromethane (G12), which are manufactured, packaged, and shipped from this plant. The manufacturing process and packaging operations, the related work and work practices, and the control measures were observed for the purpose of assessing the fluorocarbon exposure to the plant personnel.

For normal operating conditions, the greatest potential fluorocarbon exposure is associated with indoor packaging operations. Air samples, using personal samplers worn by the workers at the various work stations showed average TWA exposures to chemical operators in the manufacturing process areas to be 5.9 ppm for G11, 1.6 ppm for G12, and 0.75 ppm for CCl_4 to the Genetron operator; 7.0 ppm for G11, 1.2 ppm for G12, and 0.71 ppm for CCl_4 to the No. 2 operator; and 6.4 ppm for G11, 1.1 ppm for G12, and 0.5 ppm for CCl_4 to the HCl operator. The tank operator experienced average TWA exposures of 20.4 ppm for G11, 21.6 ppm for G12, and 1.1 ppm for CCl_4. In the packaging building the TWA exposures measured for production packaging operators ranged from 10 to 21 ppm for G11 and 1.8 to 43 ppm for G12 for the patterns of packaging operations employed during the sampling periods. The TWA exposure level for CCl_4 in the packaging building was determined to be non-detectable, i.e., <0.1ppm.

Primary control methods employed were process design and enclosure, dilution ventilation, local exhaust ventilation, and general control of process material losses. The existing control efforts are effective in maintaining worker exposures below the permissible TWA levels.

This report was submitted in fulfillment of Contract No. 210-75-0064 by Tracor Jitco, Inc., under the sponsorship of the National Institute for Occupational Safety and Health.

INTRODUCTION

Under the broad authority of the Occupational Safety and Health Act of 1970, the National Institute for Occupational Safety and Health is charged with the responsibility of conducting research, experiments, and demonstrations pertaining to occupational safety and health (1). Studies of this nature are authorized under the Occupational Safety and Health Act of 1970, set forth by the 91st Congress, S.2193, Public Law 91-596, December 29, 1970. Specifically NIOSH has been authorized responsibilities for conducting field research studies in industry, to evaluate findings and report on these findings. Section 20(a)7 states that NIOSH shall conduct and publish industrywide studies of the effects of chronic or low-level exposure to industrial materials, processes, and stresses on the potential for illness, disease, or loss of functional capacity in the aging adults. Section 20(b) further states that NIOSH is authorized to make inspections and question employers and employees as provided in Section 8 of this Act in order to carry out the functions and responsibilities under this Section. Section 20(c) further states the authority to enter into contracts, agreements, or other arrangements with appropriate public agencies or private organizations for purposes of conducting studies relating to responsibilities under the Act.

There are many chemicals used in industry for which there is insufficient data and experience to determine the long term biological effects on exposed workers. Additionally, there is a need to determine the effectiveness of control measures presently in use by industry, and to identify work practices and other control methods which would limit worker exposures to the lowest possible level.

In July 1975, Tracor Jitco, Inc., was awarded a contract to investigate three agents newly suspected as occupational health hazards. The first of the three agents specified by NIOSH was epichlorohydrin, the second, fluorocarbons. The first phase of these projects consisted of a literature review and compilation of pertinent articles. By agreement with the Project Officer, the field investigation consisted of walk-through surveys of production sites and selected user sites, and industrial hygiene surveys of these facilities. The primary purpose of the industrial hygiene survey was to determine the exposure of workers to the chemical agent and to document engineering controls, work practices, administrative controls, and biological and environmental monitoring procedures being used by the companies.

Under the contract, Tracor Jitco was also to evaluate personnel records and occupational histories of exposed workers with the purpose of duplicating such records so that they would be available to NIOSH for a possible retrospective epidemiological study. This portion of the contract has, however, been eliminated.

During the industrial hygiene survey at Allied Chemical, Specialty Chemicals Division, Danville, Illinois, air samples were collected to determine current worker exposures to chlorofluorocarbons (GENETRON(R)). This report includes a description of the plant areas where G11 and G12 are manufactured and used, the plant medical and industrial hygiene programs, air sampling and analytical methods used, sample results, and conclusions and recommendations for improvements. Industrial hygiene surveys were conducted at this facility on March 30-31, 1976, and because of difficulties in obtaining complete sample data, was resurveyed on August 23-24, 1977.

FACILITY DESCRIPTION

MANUFACTURING SITE

This Allied Chemical plant is located east of Brewer Road between Interstate 74 and Route 136 in a semi-rural area on the outskirts of Danville, Illinois. The plant is involved with the production and packaging of fluorocarbons G11 and G12 or the blending of them with other materials for shipment to customers. Packaging and blending using other fluorocarbons is also performed but to a lesser extent.

G11/G12 PRODUCTION FACILITY

This plant produces two chlorofluorocarbon products, G11 (trichlorofluoromethane) and G12 (dichlorodifluoromethane) by reacting carbon tetrachloride and hydrogen fluoride in a continuous, enclosed process. The processing equipment (reactor tower, distillation columns, piping and pumps) are located out-of-doors. A separate building adjacent to the processing structure houses the process controls and is the primary work location for the plant operators. Raw material and product storage tanks (tank farm area) are located adjacent to the production plant with railroad and roadway access.

PACKAGING FACILITY

G11 and G12 are routinely transferred from production storage to a variety of containers, i.e., from 15 lb. cylinders to 1 ton cylinders as well as truck and railroad tank cars. The tank trucks and railroad tank cars are loaded out-of-doors adjacent to the tank farm area. Other containers are routinely filled in a single story 15,000 sq. ft. building. Adjacent to this building is an out-of-doors cylinder filling facility that is used when flammable component gases are blended with the fluorocarbons.

MEDICAL AND INDUSTRIAL HYGIENE PROGRAM

MEDICAL PROGRAM

Several local physicians provide medical services under contract to the plant. Medical records are retained by the physicians except for summary reports which are provided to, and retained by, the plant with the personnel records. These have been maintained since plant start-up.

INDUSTRIAL HYGIENE PROGRAM

The plant laboratory does perform some routine air analyses. The Corporate Specialties Chemicals Division provides industrial hygiene service to the plant; Mr. Dale Shapiro is the Division Manager of Occupational Health and Toxicology. The plant safety program includes concern and responsibility for health related problems.

DESCRIPTION OF PROCESSES AND OPERATIONS INVOLVING FLUOROCARBONS

FLUOROCARBON G11/G12 MANUFACTURE

Conventional chemical processing operations are conducted out-of-doors in a totally enclosed, continuous processing system (Figure 1). The raw materials, carbon tetrachloride and hydrogen fluoride, are fed to the reactor with a catalyst. The products of the reaction flow to a strip column where the lower boiling G12 (-29.8° C at 1 atmosphere) is distilled off. The G11 is recovered from a second distillation tower. The by-product, hydrogen chloride, is recovered, purified and sold in the form of hyrochloric acid (bulk).

PACKAGING OPERATIONS

The G11/G12 products are routinely transferred from storage to a variety of containers for shipping. These vary from 15 lb. cylinders to 1 ton cylinders as well as truck and railroad tank cars. The size of the containers and the fluorocarbon (or mixture) being packaged is dependent, of course, upon demand. The smaller containers are filled indoors, one shift per day. During summer months, several work shifts may be necessary, employing seasonably available part time workers.

The containers filled include:

15, 30, and 50 lb. jugs	-	3 filling lines
1 ton cylinders	-	1 filling line
125-145 lb. cylinders	-	1 filling line
7, 8, 9, 20, and 23 lb. cylinders (G503)	-	1 filling line

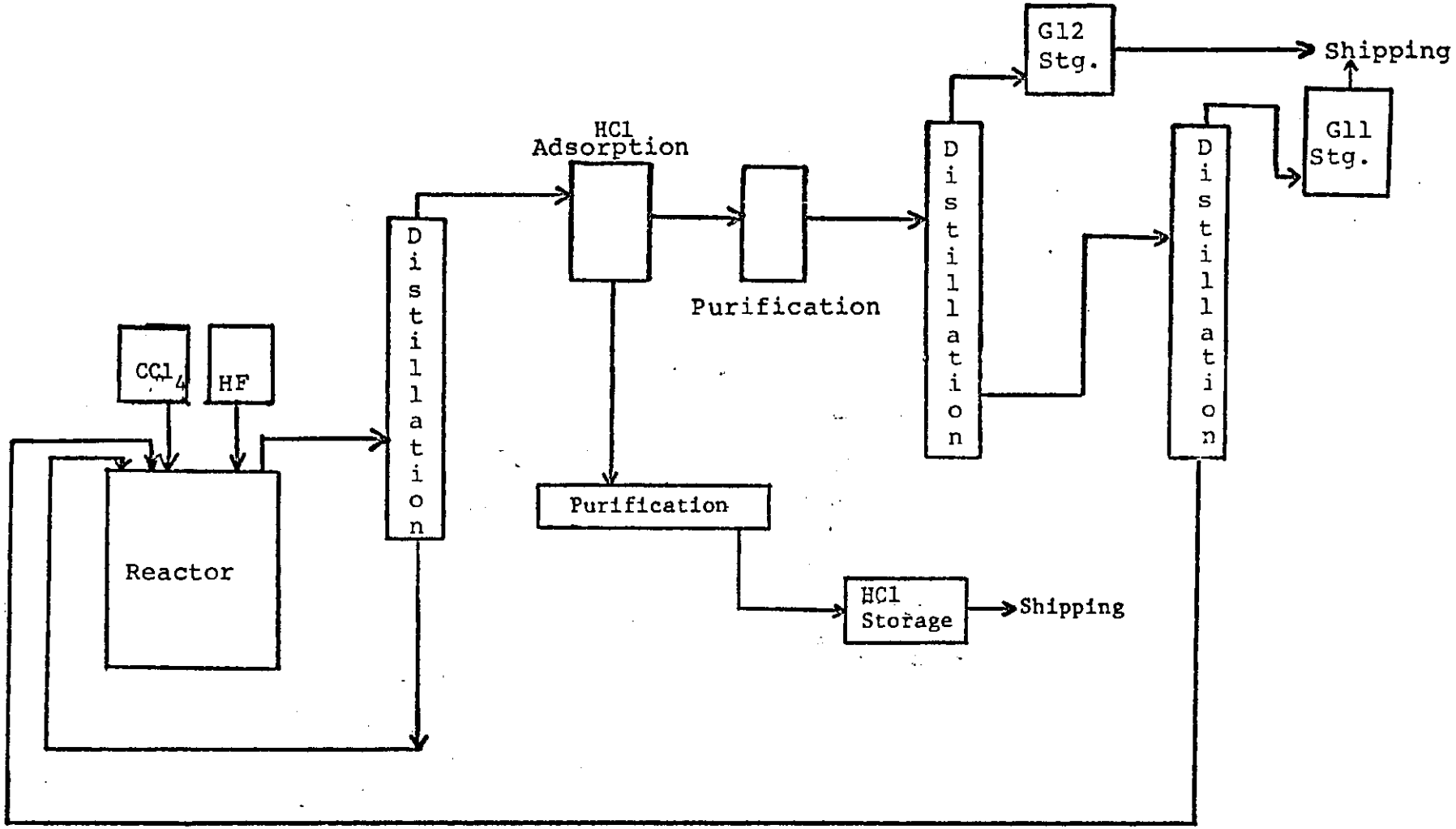
Jugs are one way containers. Returned gas cylinders are cleaned, sand blasted, and repainted according to the color code applicable for the gas or mixture being filled.

The G503 (an azeotropic mixture of G23 trifluoromethane and G13 chlorotrifluoromethane) is packaged in several sizes of smaller cylinders and in relatively small quantities.

Other mixtures are packaged according to customer orders. These mixtures or blends not only include the chlorofluorocarbons but other materials such as methylene chloride.

PRODUCTION HISTORY

Chlorofluorocarbon manufacture has been continuous at this site since 1955 with no major changes in the manufacturing process. However, products packaged and shipped from the site have increased from three basic products to



Block Flow Diagram

Danville Fluorocarbons Plant

Figure 1

many fluorocarbon blends, i.e., mixtures of G11 and/or G12 with other fluorocarbons and/or other gases as well as other fluorocarbon blends. Currently, there are 56 hourly employees; the number varies from 44 to 74. During the summer peak packaging period (3 full shifts), employment includes short-term summer employees.

G11 & G12 production (Chemical plant operators)	13	
Packaging (packagers)	14	
Tank Farm	4	
Service & Maintenance	15	
Laboratory (plant)	8	
Supervisory	19	(7 in Manager's office)

The production personnel operate the G11/G12 plant from a control room immediately adjacent to the production facility. These operators work out-of-doors or in the control room.

Laboratory personnel are in and out of the laboratory as is necessary for the collection of process and shipment samples for quality control analysis.

Tank farm personnel are out-of-doors adjacent to the production facility and are engaged in transferring the products (and blending other gases) to the tank, tank trucks, and railroad tank cars.

Packaging personnel work at various stations, depending upon orders to be filled, in a single story 120 ft. x 65 ft. building (Figure 2).

Service and maintenance personnel work throughout the plant. The production operators are responsible for shut down and preparations prior to any repair or maintenance work on process equipment.

The union contract is with the ICWU/AFL-CIO.

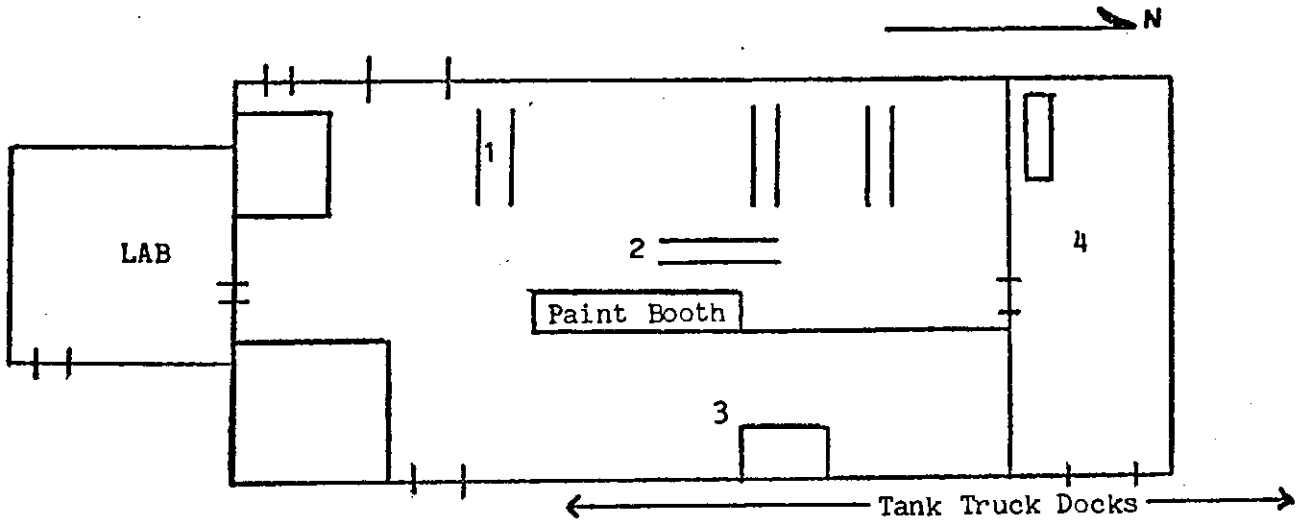


Figure 2. Packaging Building

1 - jug filling production lines
2 - cylinder packaging (large (code 165) cylinders) production line
3 - cylinder packaging (small cylinders/bottles) custom filling/low temperature condensation
4 - ton cylinder filling line

PLANT SURVEY

PAST EXPOSURES

The limited records of air sampling data collected by the plant personnel include data to determine air concentration at selected locations or to determine peak concentrations. No TWA exposure levels had been determined for the various job types prior to this study. Momentary air concentrations of the order of 1,000 ppm have been measured during packaging operations, indicating a maximum 8 hour TWA of 250-350 ppm.

The number of plant employees with exposure histories since the plant started would number about 120. Five have retired and two are known to have died. This does not include the part-time summer employees since these were short-term employement. The plant maintains personnel records and has records from the time of plant start-up.

POTENTIAL EXPOSURES

The chemical operators, tank farm workers, and maintenance personnel are potentially exposed to the raw materials and the products (see process descriptions). The packaging operators are potentially exposed to the products as well as to the raw materials being repackaged (other fluorocarbons, gases, or liquids being blended). Laboratory personnel may be routinely but intermittently exposed to products and raw materials while collecting quality control samples. However, under normal operating conditions, the predominant potential exposures exist indoors from production packaging operations where a loss of fluorocarbon and/or other blending material to the workroom is experienced repeatedly throughout the work shift.

HOUSEKEEPING

The plant environs and the buildings are maintained in a clean and orderly fashion.

CONTROL METHODS

The G11/G12 manufacturing process is essentially totally enclosed except for sampling ports and low level process leakage. The process structures are open. Loss of process materials or product is minimized as a matter of process economy. Some loss does, however, occur at each cylinder or tank filling operation when the disconnection is made. The length of the disconnect hose has been reduced to minimize the loss per disconnect. The principal control relied upon is natural dilution of these losses to the plant environment. Monitoring of air concentrations for selected operations has been done by corporate industrial hygiene personnel. A report showing results of exposure measurements to G12 and G22, and recommendations on work practice restrictions and engineering controls is contained in the Appendix.

Local exhaust ventilation of enclosures is used in the packaging building at several locations: (1) Cylinder sandblasting, (2) cylinder painting, (3) ton cylinder painting, (4) G503 filling booth where the filled cylinder is immersed in G11/dry ice to condense the filled gases. Also, two roof exhausters are used in the summer, thereby increasing the rate of dilution. The building is not crowded and provides considerable dilution volume. The loss of G11 at the condensing operation is appreciable, therefore, an enclosing booth is used to locally exhaust the evolved fluorocarbon. Visual observation indicated that there was only minimal local exhaust of the open top enclosure of the G11 cooling bath and at the spray paint booth. It is suggested that these air volumes be measured at several times during the year to provide an index of efficacy of the local exhaust ventilation systems, especially since these exhaust volumes also influence the dilution rate.

SURVEY LIMITATIONS

This industrial hygiene survey represents a one point in time evaluation of exposures to fluorocarbons, and, therefore, does not reflect possible variations in exposure due to seasonal or operational changes. The packaging operators represent the jobs having the greatest potential for routine fluorocarbon exposure. The air samples were collected during a period of normal operational procedures; if an emergency or abnormal situation occurred during the work shift, the higher exposure level should be reflected in the sample. Encountering an emergency during normal production over a sampling period of several shifts was remote and no unusual work situations were noted; therefore, the resulting exposure measurements are considered to be indicative of the normal operating conditions.

The samples also do not indicate exposures during major maintenance operations. On-stream maintenance or repair work may result in significant short term exposure unless very strict emergency procedures are used.

SURVEY PROCEDURES

During this industrial hygiene survey, air samples were collected to evaluate worker exposures to G11, G12, and CCl_4 in the manufacturing and shipping areas, and G11, G12, and G13 in the packaging building. The sampling method used in this survey was adsorption on charcoal and the analytical method was desorption and gas chromatograhic analysis. Air samples were collected during three consecutive shifts in the G11/G12 plant, and during 3 day shifts in the packaging building. The sample duration was for a selected portion of the work shift representing a total work operation cycle or for a full work shift or a significant representative portion of a full work shift.

SKC (SKC, Inc., Environmental Sciences Division, P.O. Box 55, Venetia, Pa., 15367) 150 mg charcoal adsorption tubes were used for sampling. The air sampling pumps used were SKC Model 222-351 Personal Pump and du Pont (E.I. du Pont de Nemours and Co., Inc., Applied Technology Division, Wilmington, Delaware 19898) P200 Constant Flow Sampler. The samples were analyzed in the Analytical Section, Kettering Laboratory, University of Cincinnati Medical Center.

DATA ANALYSIS AND EVALUATION

EVALUATION CRITERIA

The permissible concentrations (3) and threshold limit values (4) for plant process materials are listed below:

Fluorocarbons	ppm	mg/m^3
G11	1000	5600
G12	1000	4950
G13	---	---
G22*	1000	3500
G23	---	---
Other		
Methylene Chloride	200	720
Carbon Tetrachloride	10	65

EXPOSURE DATA

Product G11/G12 Manufacture

Table 1 shows the results of air sampling in the G11/G12 manufacturing plant and tank farm (shipping and storage) areas. Three plant operators (Genetron operator, No. 2 Genetron operator, and HCl operator) monitor the plant operations from a central process control room during each shift. The Genetron operators work in the control room and throughout the processing area. The HCl operator works in the control room and in the plant areas processing recovered HCl. The results show that these three operators have similar TWA exposure levels. Averaging the TWA exposures determined for each shift the Genetron operator experienced average TWA exposures of 5.9 ppm G11, 1.6 ppm G12, and 0.75 ppm CCl_4. The No. 2 operator experienced an average TWA exposure of 7.0 ppm G11, 1.2 ppm G12 and 0.71 ppm CCl_4. The HCl operator experienced an average TWA exposure of 6.4 ppm G11, 1.1 ppm G12, and 0.50 ppm CCl_4.

The tank farm operators work two shifts per day at the loading docks and in the tank storage area. Averaging the TWA exposures determined during 3 work shifts, the tank farm operator experienced a TWA exposure level of 20.4 ppm G11, 21.6 ppm G12, and 1.1 ppm CCl_4.

* Note: While the common TLV (1000 ppm) for these materials has been accepted as an attainable good practice level rather than as a hazardous limit (5), it should be noted that current studies indicate a possible teratogenic response in rats exposed to G22 at levels as low as 500 ppm (See Appendix.)

Table 1

Results of Air Sampling - Product Manufacturing, G11 and G12

No.	Sample Location/Job	Shift Time	Air Concentration ppm G11	G12	CCl_4
(8/23)					
1	Tank Farm Operator	1 1000-1433	17.7	15.6	0.17
2	Genetron(R) Operator	2 1450-2315	8.6	3.8	0.54
3	Genetron(R) No. 2 Operator	2 1450-2228	8.3	1.2	0.48
4	Genetron(R) HCl Operator	2 1450-2248	6.0	1.8	0.50
5	Tank Farm Operator	2 1530-2300	39.3	43.1	1.1
(8/24)					
6	Genetron(R) Operator	3 2252-0705	3.5	0.20	0.60
7	Genetron(R) No. 2 Operator	3 2252-0705	7.9	0.95	0.66
8	Genetron(R) HCl Operator	3 2252-0705	7.2	0.7	-
9	Tank Farm Operator	1 0700-1450	4.1	6.2	1.9
10	Genetron(R) Operator	1 0715-1450	5.6	0.8	1.1
11	Genetron(R) No. 2 Operator	1 0715-1445	4.8	1.4	1.0
12	Genetron(R) HCl Operator	1 0715-1445	5.9	0.9	-
	Summary TWA Exposure Levels				
	Tank Farm Operator (3 shift average)		20.4	21.6	1.1
	Genetron(R) Operator (3 shift average)		5.9	1.6	0.75
	Genetron(R) No. 2 Operator (3 shift average)		7.0	1.2	0.71
	HCl Operator (3 shift average)		6.4	1.1	0.50

Product Packaging

Table 2 shows the results of air sampling in the product packaging building when G11, G12, and other materials (depending upon custom orders and product mixes) are packed in a variety of containers, i.e. jugs, large cylinders, and small cylinders or bottles.

Large (code 165) cylinders are filled and painted on a production line located in the center of the building. Jugs (30 lb) are filled in parallel loading lines on the west side of the building. Each line may pack different materials. Cylinders, generally small cylinders, are packed with G13 or mixtures such as G502, G503, or other custom mixes in the east side of the building using a low temperature G11 condensation bath to transfer a weighed amount of gas from cylinder to cylinder.

Personal air samples were collected in this building on three different day shifts. Since the packaging operations vary, in duration and volume as well as product, with time, the conditions that result from different combinations of activities are also variable from day to day or month to month. To describe the different pattern of packaging operations observed on the three sampled shifts, the shifts have been designated as shifts A, B, and C.

During shift A the large cylinder packer (No. 1) was packing G12 and packer No. 4 was packing G13 in bottles by low temperature condensation using G11. No other materials were observed being packed during this shift. The cylinder packer (No. 1) experienced a TWA exposure of 73 ppm G12 and 15.6 ppm G11 during this shift. The cylinder packer (No. 4), while filling four bottles with G13 over a period of 35 minutes, experienced a TWA exposure of 764 ppm G11, 20.2 ppm G12, non-detectable (<0.1) ppm G13 and non-detectable (<0.1) ppm CCl_4.

On shift B the large cylinder packer (No. 1) was packing G22 while packer No. 2 was packing G12 in jugs. The cylinder packer (No. 1) experienced a TWA exposure of 11.9 ppm G12 and 6.2 ppm G11.

During shift B the jug line packer (No. 2), while packing G12 experienced a TWA exposure of 23.7 ppm G12 and 12.4 ppm G11.

During shift C cylinder packer No. 2 packed G12 in jugs, packer No. 3 packed G22 in jugs for 90 minutes, and packer No. 4 packed G503 and G13 using the G11 condensation system. Packer No. 2, while packing G12 on a jug line experienced a TWA exposure of 0.5 ppm G12 and 7.8 ppm G11. Packer No. 3, while packing G22 for 90 minutes, experienced a TWA exposure during this period of 4.7 ppm G12 and 8.5 ppm G11, Packer No. 4, while packing G503 and G13, experienced a TWA exposure of 37.5 ppm G11 and 1.9 ppm G12 for 134 minutes and 17.7 ppm G11 and 2.4 ppm G12 for 167 minutes during shift C.

Table 2. Results of Air Sampling - Product Packaging

NO.	SAMPLE JOB/LOCATION	SHIFT TIME	AIR CONCENTRATIONS ppm G11	G12	G13	CCl_4
13	Cylinder Packager No. 1/Packing Large (Code 165) Cylinders with G12. (8 hour operation)	A 1000-1516	15.6	73		
14	Cylinder Packager No. 4/Packing 23 lb bottles with G13 using G11-Dry ice bath. (Packed 4 bottles/35 min.)	A 1431-1506	764	20.2	ND	ND
1	Cylinder Packager No. 1/Packing Large (Code 165) Cylinders with G22. (8 hour operation)	B 1211-1624	6.2	11.9		
2	Cylinder Packager No. 2/Packing 30 lb Jugs with G12. (8 hour operation)	B 1202-1624	12.4	23.7		
3	Cylinder Packager No. 3/Packing 30 lb Jugs with G22. (1 1/2 hour operation)	C 0814-0944	8.5	4.7		
4	Cylinder Packager No. 2/Packing 30 lb Jugs with G12. (8 hour operation)	C 0810-1623	7.8	0.5		
5	Cylinder Packager No. 4/Packing 9 lb and 20 lb bottles with G503 using G11-Dry ice condensation bath. (2 1/2 hr. operation)	C 0946-1200	37.5	1.9		
6	Cylinder Packager No. 4/Packing 23 lb bottles with G13 using G11-Dry ice bath. (4 hour operation)	C 1202-1547	17.7	2.4		
	Summary TWA Exposure Levels					
	Cylinder Packager (#1) (2 sample ave.)		11	43	-	-
	Cylinder (Jug)Packager (#2) (2 sample ave.)		10	12	-	-
	Cylinder (Bottle) Packager (#4) (time-weighted ave. 6 1/2 hr. operation)		21	2	N.D.	N.D.

RECOMMENDATIONS

Since all measurements show the TWA exposure levels for normal operations to be considerably less than the levels specified in the standards, the existing control efforts are effective and should be maintained.

Though not observed, during abnormal work situations which have higher potential for exposure such as occurrence of process leaks or repair or maintenance on the processing or packaging system, special care should be taken to prevent excessive exposures.

The loss of G11 from the low temperature bath to the building atmosphere and the resulting exposures to G11 could be reduced appreciably by better use of the enclosure provided. The effectiveness of the exhaust provided varies with the degree of enclosure. The top and the side of the enclosure should be kept closed to the extent possible.

The efforts to restrict work practices of female employees of child-bearing age to prevent any inadvertant exposure to G22 should be continued as a preventive measure until further toxicologic information clarifies the degree of hazard to this group at risk.

Chilling of sample cylinders with dry ice is recommended rather than using a spray of material being sampled as reported to occur in tank truck sampling.

REFERENCES

1. Public Law-91-596, Sec. 20(a)91, Occupational Safety and Health Act, 1970.

2. Report of Plant Visit to Allied Chemical (Specialty Chemicals Division), Danville, Illinois, June 10, 1976, Tracor Jitco, Inc., NIOSH Contract 210-75-0064.

3. 29CFR Paragraph 1910.93.

4. American Conference of Governmental Industrial Hygienists, Threshold Limit Values for 1976, ACGIH, 1976.

5. American Conference of Governmental Industrial Hygienists. Documentation of the Threshold Limit Values for Substances in Workroom Air. 3rd Edition. 1971.

APPENDIX

SPECIALTY CHEMICALS DIVISION

OCCUPATIONAL HEALTH

Industrial Hygiene Survey for Genetron® 22 and 12 Exposure at the Danville Plant Danville, Illinois

by D. M. Shapiro*

SUMMARY

Personal monitoring and area samples for Genetron® 22 and Genetron® 12 were taken on April 5 and 6, 1977, at the Danville Plant, Danville, Illinois. Exposure to both materials were within current allowable exposure limits. Recent toxicological data indicate that Genetron® 22 has a weak teratogenic response in rats. The extrapolation of this data to man is not clear. Further studies are in progress to define an "acceptable" exposure limit for female employees. Recommendations on work practice restrictions and engineering controls are included.

*Work done by D. M. Shapiro and R. J. Hunt

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INTRODUCTION

An industrial hygiene survey was conducted on April 5 and 6, 1977, to determine G-22 exposures to workers in the Danville plant Danville, Illinois. The gas chromatographic analytical method yielded analysis for G-12 as well as G-22, therefore, exposures to both materials are reported.

CONCLUSIONS

The following conclusions are based on observations and measurements made during this survey. If operating conditions or process changes occur, some of these may become invalid.

1. All Genetron® 22 and 12 exposures are within current allowable limits.

2. Recent experiments at duPont's Haskell Laboratory indicate that Genetron® 22 elicits a weak teratogenic response in rats. Until further studies are completed, the extrapolation of this data to man and the choice of a lowered acceptable exposure value is not clear.

RECOMMENDATIONS

1. Until further toxicological data is recieved on Genetron® 22, the following procedures should be followed:

a) Female employees of child-bearing age should continue to be barred from G-22 packaging areas.

b) Female employees are permitted to function as lab analysts providing that they wear air-supplied respirators during sampling

operations when in the packaging and truck loading areas. As an alternative, samples of G-22 outside the lab may be taken by the male employees on the shift.

c) Female employees are permitted to enter the G-22 packaging areas (for janitorial or other purposes) one hour after filling operations are ended providing no cylinders are venting inside the building.

2. Sampling for quality control purposes should be reviewed. Engineering and work practice controls which reduce operator exposure and environmental releases should be implemented.

3. A proposed ventilation control system for the filling operations was drawn up by SCD engineering (T. Roubo). This package should be installed to help reduction of G-22 exposure levels. This system will also enable Danville works to safely handle other Genetron® fluorocarbons which may become important in the future (i.e. G-31, G-21).

4. The feasibility of reducing product loss and exposures during tank truck loading operations are under investigation by SCD engineering.

DISCUSSION

Description of Operation

Genetron® 22 is manufactured at Allied's Baton Rouge and Elizabeth plants and shipped to Danville in bulk tank cars. G-22 is repackaged primarily into 15, 25, and 50 pound jugs and into tank trucks. Some ton cylinders and 150 pound cylinders are also shipped.

Jug and 150 pound cylinder filling operations take place in the packaging building. On the day of the survey the weather was cool and doors and windows were generally closed. Therefore, G-22 concentrations measured were typical of winter operations. Much lower levels would be anticipated during the summer months when doors and windows would be opened.

Sampling and Analysis

Air samples for G-22 and G-12 were collected in Saran plastic bags.

Personal monitoring was performed by attaching a 10 liter Saran bag to a Sipon low flow rate pump operating in the push-pull mode. A tube attached to the suction side of the pump was fastened so as to draw air from the operators' breathing zone. The bag/pump assembly was placed in a backpack unit which was worn by the operator. These samples represent true time-weighted average conditions to which the operators were exposed during the sample period.

Area and breathing zone "grab" samples were taken by filling 5 liter Saran bags using a rubber squeeze bulb apparatus. These samples are used to measure point-in-time exposure levels and are helpful in evaluating items such as sources of exposure, peak exposures, or background contaminant levels.

Samples were analyzed using gas chromatography with flame ionization detection. A 6 foot Poropak Q column was used at 100°C. A 1.0 ml sample was injected using a Pressure-Lok gas tight syringe.

Calibration standards were made daily by injecting known amounts of pure G-22 or G-12 into 10.0 liters of pure nitrogen. The plant's

chromatograph was used and on the days surveyed, the detection limits were 8-9 ppm for G-22 and 22-26 ppm for G-12.

HEALTH HAZARD SUMMARY

Genetron® 22 (chlorodifluoromethane)

High concentrations of G-22 produce stimulation and then depression of the central nervous system. Narcosis occurs at approximately 200,000 ppm and mortality results at 300,000 to 400,000 ppm.

Long-term exposures to rats, mice, and rabbits at 14,000 ppm produced alterations in body weight, physiological endurance and hematological characteristics; pathological changes were noted in the lungs, central nervous system, heart, liver, kidney, and spleen. No effects were noted at 2000 ppm.

Cardiac sensitization can be evoked in dogs at 50,000 ppm, but not at 25,000 ppm.

Recent studies by duPont's Haskell Laboratory indicate that at levels as low as 500 ppm, G-22 caused a weak teratogenic response in rats. Further experimentation is underway to establish a no-effect level.

Until further tests are completed, no Allied internal Guideline is recommended.

Genetron® 12 (dichlorodifluoromethane)

Repeated exposures of animals to high concentrations of G-12 (20% by volume) caused generalized tremor, other symptoms of mild narcosis, and slight blood changes, but no pathological changes.

Concentrations up to 20% are considered safe for a single human exposure.

The Threshold Limit Value of 1000 is chosen as an attainable "good practice" value rather than as a hazard limit.

Allowable Limits

The current TLV's* for G-22 (chlorodifluoromethane) and G-12 (dichlorodifluoromethane) are 1000 ppm. This refers to an 8-hour time-weighted average exposure to which it is believed workers may be repeatedly exposed, day after day, throughout a working lifetime with no adverse effect. The OSHA standard for G-12 is also 1000 ppm. There is no OSHA standard for G-22.

Presentation of Results

Results of personal monitoring for G-22 and G-12 are shown in table 1. All time-weighted average exposures to G-22 and G-12 were within the current allowable limits (1000 ppm).

Results of area "grab" samples are shown in table 2.

This data supports the hypothesis that the highest exposure potential occurs in the jug and cylinder filling room. Much lower exposures occur in the laboratory with the highest (peak) exposures to laboratory workers occurring during sampling operations.

Tank farm workers' exposure is mainly due to the decoupling and subsequent draining of the filling hose. Due to the frequency of filling G-22 trucks, the tank farm operators' TWA exposure to G-22 would probably be less than the cylinder packager operator, but greater than the lab analyst.

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*American Conference of Governmental Industrial Hygienists, 1976.

Concentrations of G-22 1/2 hour after the shift were significantly reduced to barely detectable levels.

SOURCES OF EXPOSURE/CORRECTIVE ACTION

Jug and Cylinder Filling Operations

After jugs and cylinders are filled the valves are closed on the container and on the product line. During disconnection the refrigerant trapped between the valves is vented into the work area. A plan for reducing exposures by installing a ventilation system has been developed by SCD engineering (figures 1 and 2). This system will substantially reduce Genetron® exposure levels which is important for G-22 operations as well as in the event other fluorocarbons with lower allowable limits become commercially important (i.e. G-31, G-21).

Quality Control Sampling

Sampling of the jug and cylinder filling operations will represent low exposure potential to laboratory personnel after the above ventilation controls are added. Tank truck sampling involves chilling the sample cylinder with a spray of the material. This practice results in peak exposure to lab personnel as well as an environmental release. The feasibility of improving this technique should be investigated.

Dale M. Shapiro

D. M. Shapiro, Sr. Specialist
Industrial Hygiene

TABLE 1

SUMMARY OF PERSONAL MONITORING FOR G-22 & G-12

Date	Name	Job Classification	Description/Comments	Concentration ppm (v/v) G-22	G-12
04/05/77	J. Schroder	Cylinder Packager	7:10 AM - 2:10 PM	195	56
			2:15 PM - 3:15 PM	259	28
			TWA Exposure =	203	53
04/05/77	W. Mosby	Clinder Packager	7:18 AM - 11:47 AM	286	100
			12:45 PM - 3:10 PM	223	28
			TWA Exposure =	259	69
04/05/77	H. Reed	Cylinder Packager	7:24 AM - 11:55 AM	182	56
			1:15 PM - 2:57 PM	205	22
			TWA Exposure =	188	47
			All 3 jug lines filling G-22 on 04/05/77.		
04/06/77	H. Reed	Cylinder Packager	7:10 AM - 10:25 AM	173	43
			Only one G-22 line running until 10:25 AM - switchover to G-12 filling in PM.		
	E. Dryer	Lab Analyst	7:15 AM - 11:20 AM	8	26
			11:35 AM - 3:20 PM	Lost Sample	
			TWA Exposure =	8	26
	J. McMasters	Lab Analyst	7:25 AM - 11:15 AM	ND	ND
			11:40 AM - 3:15 PM	ND	26
			TWA Exposure =	ND	< 26
	T. Seilahymer	Tank Farm Operator	3:15 PM - 3:57 PM	333	43
			Loading G-22 truck		

TABLE 2

Summary of Grab Samples for G-22 & G-12

April 5, 1977

Description		Concentration, ppm G-22	G-12
North Jug Line			
5 min. after leak	(7:45 AM)	432	28
10 min. after leak	(7:50 AM)	355	89
Normal operations -	11:00 AM	78	122
	2:15 PM	277	33
Center Jug Line			
Normal Operations -	11:20 PM	159	267
	2:45 PM	236	33
South Jug Line			
Normal Operations -	9:15 AM	277	133
	11:30 AM	170	344
Center of Building -	11:10 AM	77	356
After Shift (1/2 hour) -	3:35 PM	14	ND*
Laboratory			
	9:55 AM	18	44
	2:00 PM	9	44

* Not detectable - limit of detection = 22 ppm

TABLE 2 (cont'd)

Summary of Grab Samples for G-22 & G-12

April 6, 1977

Description	Concentration, ppm G-22	G-12
South Jug Line		
Filling G-22 jugs (8:25 AM)	110	86
Filling G-22 Jugs (9:30 PM)	154	17
15 min. after switch to G-12 filling (10:40 AM)	27	34
Filling G-12 jugs (11:10 AM)	8	336
Walk through center of room (8:40)	47	112
Laboratory (2:02 PM)	ND	ND
Sampling G-22 in Packaging Area (E. Dryer-Breathing Zone)	235	95

April 7, 1977

Sampling G-22 truck J. McMasters - breathing zone	246	ND

TABLE 3

Summary of Exposures by Job Classification

Danville, Illinois - April 5 & 6, 1977

Job Classification	TWA Expousre, ppm G-22	G-12
Cylinder Packager	210	53
Lab Analyst	< 8 (1)	< 26
Tank Farm Operator	30 (2)	NC (3)

(1) < - Less than value indicates that some exposures were "not detected." This value averages the limit of detection (rather than zero) into the exposure calcuation.

(2) Assumes one G-22 tank truck per shift. Value would approximately double for two trucks per shift.

(3) Not calculated - exposure to G-12 throughout workshift was not measured.

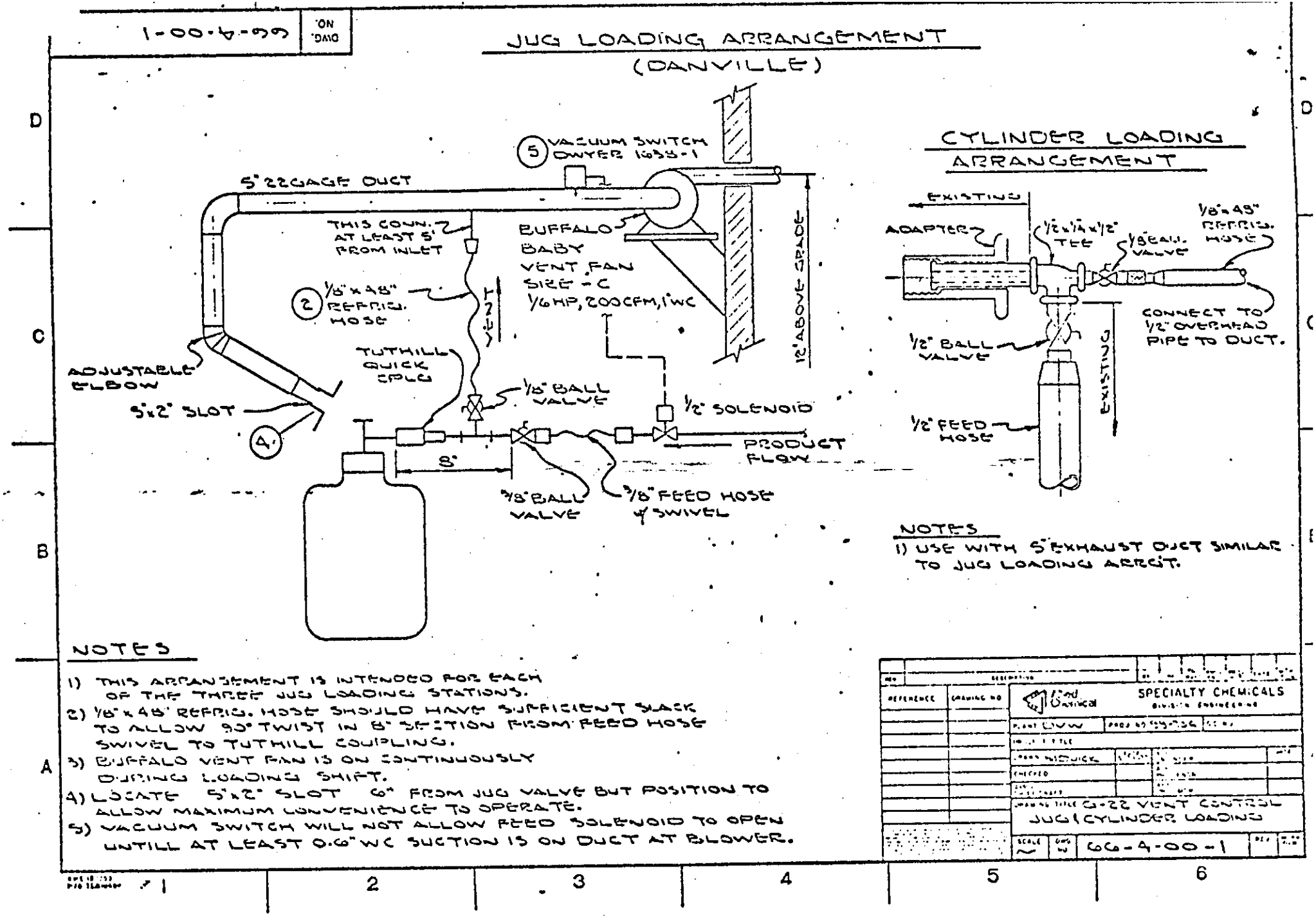
DWG. NO. 66-4-00-1
JUG LOADING ARRANGEMENT
(DANVILLE)
5" 22GAGE DUCT
5 VACUUM SWITCH DWYER 1639-1
THIS CONN. 2' AT LEAST 5' FROM INLET
BUFFALO BABY VENT FAN SIZE - C 1/6 HP, 200 CFM, 1"WC
2 1/8" x 48" REFRIG. HOSE
12" ABOVE GRADE
ADJUSTABLE ELBOW
5"x2" SLOT
4
TUTHILL QUICK CPLG
1/8" BALL VALVE
1/2" SOLENOID
PRODUCT FLOW
8"
3/8" BALL VALVE
3/8" FEED HOSE W/ SWIVEL
CYLINDER LOADING ARRANGEMENT
EXISTING
ADAPTER
1/2"x1/4"x1/2" TEE
1/8" BALL VALVE
1/8" x 48" REFRIG. HOSE
CONNECT TO 1/2" OVERHEAD PIPE TO DUCT.
1/2" BALL VALVE
1/2" FEED HOSE
EXISTING
NOTES
1) USE WITH 5" EXHAUST DUCT SIMILAR TO JUG LOADING ARRGT.
NOTES
1) THIS ARRANGEMENT IS INTENDED FOR EACH OF THE THREE JUG LOADING STATIONS.
2) 1/8" x 48" REFRIG. HOSE SHOULD HAVE SUFFICIENT SLACK TO ALLOW 90° TWIST IN 8" SECTION FROM FEED HOSE SWIVEL TO TUTHILL COUPLING.
3) BUFFALO VENT FAN IS ON CONTINUOUSLY DURING LOADING SHIFT.
4) LOCATE 5"x2" SLOT 6" FROM JUG VALVE BUT POSITION TO ALLOW MAXIMUM CONVENIENCE TO OPERATE.
5) VACUUM SWITCH WILL NOT ALLOW FEED SOLENOID TO OPEN UNTILL AT LEAST 0.6" WC SUCTION IS ON DUCT AT BLOWER.
Union Carbide
SPECIALTY CHEMICALS
G-22 VENT CONTROL
JUG/CYLINDER LOADING
66-4-00-1

Figure 1

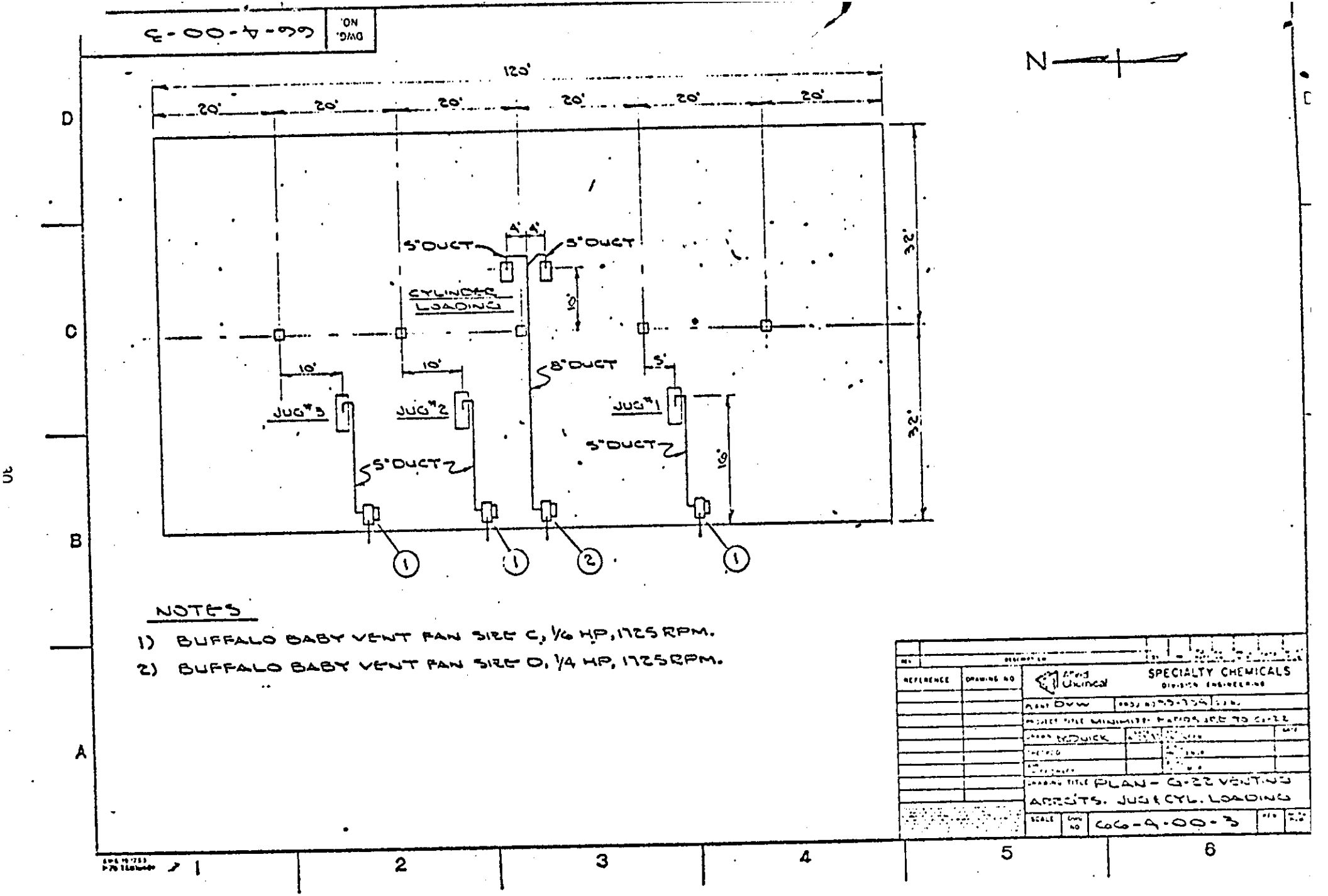
120'
20'
20'
20'
20'
20'
20'
32'
32'
D
C
B
A
5" DUCT
5" DUCT
4'
4'
CYLINDER LOADING
10'
10'
10'
5'
8" DUCT
JUG #3
JUG #2
JUG #1
5" DUCT
5" DUCT
10'
1
1
2
1
N
NOTES
1) BUFFALO BABY VENT FAN SIZE C, 1/6 HP, 1725 RPM.
2) BUFFALO BABY VENT FAN SIZE D, 1/4 HP, 1725 RPM.
SPECIALTY CHEMICALS
PLAN - G-22 VENTING
ARRGTS. JUG & CYL. LOADING
666-A-00-3
1
2
3
4
5
6

Figure 2