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CENTER FOR DISEASE CONTROL
NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH
CINCINNATI, OHIO 45226

HAZARD EVALUATION AND TECHNICAL ASSISTANCE
REPORT NO. TA 79-14

CONTAINER GRAPHICS CORPORATION
TOLEDO, OHIO

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Study Requested By:
Mr. Leo Leonard, Occupational Health Officer
Division of Occupational Health
State of Ohio

Study Conducted By:
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I. SUMMARY

On January 4, 1979, the National Institute for Occupational Safety and Health received a request to provide sampling and analytical assistance to the State of Ohio, Division of Occupational Health, for a determination of iodine vapor in the photopolymer plate processing area of The Container Graphics Corporation, Toledo, Ohio. The request generated the development of a new and reliable method for sampling and analysis of iodine.

The conclusions and recommendations presented in this report are based on environmental measurements, observation of the work practices, ventilation measurements, professional judgement, and review of medical data and current literature.

On April 5, 1979, airborne concentrations of iodine were measured in the workers' breathing zone and in the general work area. Two of five short-term iodine samples were above the Threshold Limit Value of the American Conference of Governmental Hygienists, and the Permissable Exposure Limit of OSHA. In addition, perchloroethylene, a solvent used by plate processors, was measured with values of 100-125 ppm, which is in excess of NIOSH's recommended ceiling value of 100 ppm.

One of the two workers interviewed reported symptoms of nose congestion, and throat irritation. These symptoms are consistent with the toxicology of iodine and solvent vapor exposure. The same worker also had a rash on his left forearm which NIOSH industrial hygienists thought was contact dermatitis caused by **acrylate** monomer exposure.

This report contains recommendations to improve working conditions and ensure worker safety and health.

II. EVALUATION

A. Process Description

The Container Graphics Company processes relief graphic plates which are used to print instructions or logos on shipping containers. This process is accomplished in two rooms (Figure 1). Room 1 is the primary workroom for photopolymer plate processing. Room 2 is the iodine-dipping, finishing, and shipping area. All plates are manufactured by two employees who usually work the day shift.

The photopolymer plates are of two types: Cyrel®, manufactured by Dunlop; and Flexlite®, manufactured by UniRoyal. Each plate is cut to size, and a print or logo matt is taped over the plate. It is then put under an ultraviolet exposure unit for approximately 10-15 minutes where exposed portions of the plate are photopolymerized. The photopolymerized plate and matt are separated, and the plate is put into an enclosed plate-washing tank. The tank contains a solution of 95 percent perchloroethylene and 5 percent butyl alcohol. Inside the platewashing

tank is a rotating drum that holds the plates while solvents and brushes remove the unpolymerized monomer. When the desired relief and sharpness of the graphic plate is achieved it is removed from the tank, and excess monomer is hand wiped off with a solvent-soaked (perchloroethylene), rag. The plate is then put into a drying oven to evaporate solvents. After drying the plates are fixed with either a chlorine or iodine solution. The chlorine solution contains hydrochloric acid, bleach, and water. The solution is wiped on the Flexlite plate, then rinsed with water and dried.

The Cyrel plate is hand-submerged into the iodine solution, which is in a 30 inch by 40 inch by 6 inch fibrous glass container. The iodine solution contains powdered iodine, potassium iodide, and water. After a few minutes the plate is removed, and while holding the plate above, the excess iodine solution is allowed to drip back into the container. The plate is then dried in the oven and prepared for shipping.

The chlorine solution and iodine solution help to preserve the life of the plate.

Approximately eight to nine photopolymerized plates are manufactured each day. The amount of chlorine or iodine fixing of plates varies from day to day. During the NIOSH evaluation only two plates were iodine fixed.

Each employee has an equal responsibility in manufacturing the photopolymerized graphic plates.

B. Evaluation Design

1. Since the State of Ohio, Division of Occupational Health, requested NIOSH's technical assistance for only the analytical and sampling method for development of iodine vapor, the primary focus of sampling was on iodine. However, NIOSH investigators did take ventilation measurements, screen for organic solvents, hand out questionnaires, and conduct personal interviews to more thoroughly evaluate the potential health hazards in this company.

2. Iodine Analytical and Sampling Method Development: The analytical and sampling method development for iodine was the primary responsibility of Measurement Support Services (MSS) of NIOSH.

A bulk solution from Container Graphics Company was submitted to MSS for analytical and sampling method development. The following report describes the laboratory procedure.

For the bulk sample, a titration method was used to determine the concentration of iodine in the sample solution. One milliliter (mL) of sample solution was titrated against standardized 0.020 N sodium thiosulfate solution. An average concentration of 2.81 milligrams of iodine per milliliter of sample solution was obtained from triplicate titrations.

The accuracy of the titration method was checked by titrating 1.0 mL of 0.020 N iodine solution against the standard 0.020 N sodium thiosulfate that was used for titration of the sample. From triplicate analyses the precision was ± 5%. For the titrations a Class A microburet (± 0.005 mL) was used with 1.0 mL of starch indicator solution per analysis.

Then, the effect of potassium fluoride on the titration of iodine was studied. To 1.0 mL of 0.02 N iodine solution, 65 mg of potassium fluoride was added and the iodine concentration was determined by titrating as above. No change in iodine concentration was observed from four runs. In the next experiment the amount of potassium fluoride was increased to 325 mg - again no change in the iodine concentration was observed from 4 runs.

To develop a sampling medium for collection of iodine in air, a sampling tube was made with 100 mg of an impregnated charcoal. A sampling pump was used to collect iodine vapor on the tube by using a funnel inverted over iodine crystals. Air was pulled for about 2 hours and the iodine vapor was collected on the impregnated charcoal.

Collected iodine was desorbed from the charcoal using 10 mL of 0.005 M sodium carbonate, and 20 minutes of ultrasonication. The sample was filtered through a 0.45 µm mixed cellulose acetate filter, and the filtrate was analyzed for iodide by ion chromatography.

A broad peak was obtained by ion chromatography with a retention time of about 25 minutes. A sodium iodide solution with the concentration of 100 µg/mL iodide gave the same shaped peak at the same retention time. Thus the peak obtained from the impregnated charcoal sample was identified as iodide on the basis of retention time. After the identification of iodide peak, the chromatographic parameters were optimized to determine the feasibility of analyzing iodine as iodide by ion chromatographic method.

Three stock 1000 µg/mL iodide solutions were prepared using 1.18130 g of sodium iodide per liter of three different matrix solutions - water, 0.005 M sodium carbonate, and 0.01 M sodium carbonate. Each of these stock solutions were diluted in the same matrix solution and injected into the ion chromatograph to determine any difference in the iodide peak. No difference was observed from these matrix solutions. The areas under the peaks and the retention times were the same.

Then, the phase equilibrium desorption study was carried out by spiking the charcoal with iodide and analyzing the desorbed solution. Onto each of 100 mg portions of charcoal, 100 µg and 50 µg of iodide were added and allowed to sit for one and a half hour. Iodide was desorbed and analyzed - no apparent loss of iodide onto charcoal was observed.

For the determination of the low limit of quantitation, a series of working standards were injected and a calibration curve was obtained. For the range up to 10 µg/mL iodide the standard curve was linear. The instrument parameters were as follows:

Instrument	-	Dionex Ion Chromatograph Model 14
Anion Columns	-	3 X 125 mm Precolumn 3 X 250 mm Separator 6 X 250 mm Suppressor
Eluent	-	0.01 M Sodium Carbonate
Flow Rate	-	184 mL/hr.
Meter Scale	-	3 or 1 µ mho

The lowest standard concentration was 1 µ g/mL iodide at 3 µ mho scale. Thus, 5 µ g of iodide per sample would be the low limit of quantitation using 5 ml of desorbing solution. This is equivalent to 2.5 µg of iodine per sample.

Thus it appears that the iodine can be collected on an impregnated charcoal and converted iodide can be analyzed by the ion chromatographic method. This new method has an analytical accuracy greater than 90 percent and a precision of plus or minus 5 percent.

3. Iodine Environmental Sampling: Thirteen personal breathing zone and general area samples were obtained at Container Graphics Company to determine iodine vapor levels. The samples were obtained with portable personal vacuum pumps operating at 600 cubic centimeters per minute, or at 1.0 liter per minute. The adsorbing media for Iodine vapor was impregnated charcoal in glass tubes; a prefilter was attached to capture iodide salts.

Five short-term and eight long-term iodine vapor samples were taken during the NIOSH survey. Normally, long-term samples are not taken when there is a ceiling concentration; however, NIOSH industrial hygienists did so to test the new iodine sampling method sensitivity and to obtain more recordable iodine vapor concentrative data.

4. Iodine Sampling Analysis: Analysis of iodine collected at the Container Graphics Corporation was performed in the following manner:

Each charcoal tube was broken open and the impregnated charcoal was transferred to a centrifuge tube. Iodine, converted to iodide by the impregnated charcoal, was desorbed with 5 mL of 0.01 M sodium carbonate and each sample was allowed to sit for one hour. Then, the samples were

desorbed with ultrasonication for 10 minutes, and filtered through a 0.3μm mixed cellulose acetate filter. Collected filtrate was analyzed for iodide by ion chromatography.

The analytical standards were prepared by diluting stock 1000μg/mL iodide solution with 0.01 M sodium carbonate. The standards covered the analytical range up to 10μg/mL. These standards were injected into the ion chromatograph and a linear standard curve was obtained. The peak height of each sample was measured and compared against the standard curve. The instrumental parameters were as follows:

Instrument	- Dionex Ion Chromatography Model 14
Anion Columns	- 3 X 125 mm Precolumn 3 X 250 mm Separator 6 X 250 mm Suppressor
Eluent	0.01 M sodium carbonate
Flow Rate	- 184 mL/hr.
Meter Scale	- 30μ mho
Recorder	- 50 mV scale

The results are reported in Table I. The units are micrograms of iodine per tube. The lower limit of quantitation was 2 micrograms of iodine per sample.

Quality control data for the analysis was obtained by spiking iodide solutions to four 100 mg portions of impregnated charcoal. These quality control samples were analyzed in the same manner as the field samples. An average recovery of 99% was obtained with 6% relative standard deviation.

5. Perchloroethylene vapor concentrations from platewashing operations were measured by Drager colorimetric indicator tubes. Chlorine gas was monitored also by Drager tube during the plate fixing operation.

Ventilation measurements were taken at the exhaust grill, chlorine wash table, and iodine solution tank area. Smoke tubes were also used to characterize the air currents in the two plate making rooms.

The two employees were given non-directed, NIOSH-designed medical questionnaires, which were returned during the evaluation. One employee was subsequently interviewed by a NIOSH industrial hygienist as a result of his responses on the questionnaire.

C. Recommended Criteria

There are three sources of criteria commonly used to evaluate toxic air contaminants in the workplace; (1) NIOSH criteria documents for Recommended Occupational Health Standards[1], (2) Proposed and Recommended Threshold Limit Values (TLVs) for the American Conference of Governmental Industrial

Hygienists (ACGIH)[2], and (3) Department of Labor Standards[3] enforced by the Occupational Safety and Health Administration. These values are based on the current state of knowledge concerning the toxicity of the specific substances and are derived from available animal and human toxicity data and industrial experience. These levels are values to which it is believed that nearly all workers may be exposed for an 8-hour day, 40-hour workweek, over a working lifetime. However, because of a wide variation in individual susceptibility, a small percentage of workers may experience discomfort from some substances at concentrations at or below the recommended level; a smaller percentage may be affected more seriously by aggravation of a pre-existing condition or by development or an occupational disease.

Substance	(1) NIOSH P.P.M*	(2) ACGIH P.P.M.*	(3) OSHA P.P.M.*
Chlorine	0.5[1]	1.0	1.0
Iodine	----**	0.1[1]	0.1
Perchloroethylene (tetrachloroethylene)	50.0	100.0[2]	100.0

* Parts of contaminant per million parts of air. As an 8-hour Time Weighted Average (TWA) daily exposure.
** Notation indicates that substance has no existing occupational exposure criteria or standard.

1. Ceiling value, for a 15-minute exposure, not to be exceeded.

2. Substance can be absorbed through skin, mucous membranes, or eye, either airborne or by direct contact.

The following toxicology summaries are presented to familarize the worker with the effects of exposure to these substances.

1. Chlorine

Chlorine is the commonest of the four halogens, which are among the most chemically reactive of all the elements. The local harmful effects of chlorine occur because it reacts with body moisture to form acids. It can be extremely irritating to skin, eyes, and mucous membranes, and may cause corrosion of teeth. Prolonged exposure can cause chloroacne.

The systemic harmful effects of high concentrations of chlorine include asphyxiation caused by larynx muscles cramping, nausea, vomiting, anxiety, and syncope. Acute respiratory distress has been recorded, which can develop into tracheobronchitis, pulmonary edema, and pneumonia.[4]

2. Iodine

Iodine, like chlorine, is a strong irritant. Irritation rather than systemic action limits the concentrations of iodine vapor which can be tolerated.[5] Even in low concentrations it is irritating to the respiratory tract, eyes, and to a lesser extent, the skin.[6] Concentrations as low as 0.1 ppm in the air (the current TLV ACGIH and PEL OSHA) may cause eye irritation upon prolonged exposure.[7] Concentrations higher than 0.1 ppm will cause irritation of the respiratory tract and, ultimately, pulmonary edema.[8] Chronic absorption of iodine causes "iodism" (more commonly called hyperthyroidism), a disease characterized by tachycardia, tremor, weight loss, insomnia, diarrhea, conjunctivitis, rhinitis, and bronchitis.[9] In addition, hypersensitivity to iodine may develop, characterized by skin rashes and possibly rhinitis and/or asthma.[6] Elemental iodine precipitates protein and can continue to penetrate and damage the skin.[10] Industries that use both iodine and solvents (such as perchloroethylene) should warn employees of the synergistic effects of skin cell permneability caused by the interaction of the above agents. The uses of iodine in industry include the synthesis of organic chemicals, pharmacology, photographic film, making of drystuffs, and most recently, the graphics industry. Because it is a powerful oxidizing agent it can explode when in contact with acetylene or amnonia.[6]

Iodine has a characteristic odor and a sharp and acrid taste. Its vapor is violet and corrosive, and can color the skin.[11]

3. Perchloroethylene (tetrachloroethylene)

Perchloroethylene, a widely used solvent in industry, is a colorless, heavy liquid with an ethereal odor. It's odor can be detected at 50 ppm. The harmful effects range from scaly and fissured dermatitis to paralysis of hands and feet. Clinical symptoms include fatigue, headache, constipation, insomnia, anorexia, and nausea. Excessive exposure can cause pulmonary edema. Since perchloroethylene is a well known central nervous system depressent, NIOSH has recommended that the environmental limit for perchloroethylene have a time-weighted-average concentration of 50 ppm. This limit should prevent neurologic effects as well as eye and respiratory tract irritation.[1] A ceiling value of 100 ppm by NIOSH was recommended because human exposures to concentrations between 100 and 300 ppm have resulted in neurologic effects such as impaired motor coordination.[1]

III. Evaluation Results, Discussion and Recommendations

A. The results of environmental sampling are contained in Tables 1 and 2. NIOSH has not evaluated the health effects of iodine vapor exposure to date, but the ACGIH and OSHA have set environmental limits for iodine at 0.1 ppm as a ceiling value. Whenever the exposure limit or recommended exposure limit is exceeded NIOSH makes recommendations to minimize these exposures.

Two short-term samples, one personal and one general area, exceeded the exposure limit for iodine as recommended by the ACGIH and set by OSHA. Two other short-term samples taken in the same area had concentrations that were one half the standard. The variability in iodine exposure (i.e., iodine concentrations above the standard compared to those below), may be related to work practices as well as to poor ventilation control.

Ventilation controls for iodine vapor were virtually non-existant. An exhaust grill located 4 feet to the left and above the iodine tank had no effect on effectively capturing iodine vapor. Smoke from a smoke tube emitted near the iodine container was almost stagnant, with vary slow dispersion toward the grill. A thermometer measured 0-10 fpm at the iodine container lid.

The Container Graphics Company has taken steps toward controlling environmental exposure to iodine. For example, to contain iodine vapors the company has installed a clear plastic containment curtain around the iodine tank. They have also installed a flip lid on the tank. The flip lid on the iodine tank seemed to contain iodine vapors when plates were not being dipped, (and our long term air samples support this). However, we did notice violet stains on the containment curtain and walls next to the tank in room 2. Thus suggesting that iodine vapor exposure is short but intense.

Workers were also provided personal half-face organic vapor and acid gas respirators (cartridge R25, Wilson, and mask R635, Wilson) for use when dipping plates in iodine or when fixing chlorine solution. However, no instructions were given on maintaining, operating, and storing of these respirators. One worker had used masking tape to repair a cracked organic vapor and acid gas cartridge. This was the same worker who complained of nose congestion and throat irritation. (The NIOSH industrial hygienist advised the worker to replace the cartridge immediately.)

Perchloroethylene vapor and chlorine gas concentrations were monitored with Drager tubes to spot check contaminant levels during specific operations in the plate processing room. Exposures to perchloroethylene occured primarily during removal of plates from the platewashing tank and during solvent wipedown of plates. The tank had a local exhaust system with a 4-inch-diameter hole cut into the back. When the tank lid was closed and plates were being washed, solvent vapors were adequately captured. This was determined by smoke from smoke tubes being drawn into the tank through the lid gasket. However, when the lid was opened and the plates removed, solvent vapors from the tank and from the plates were easily detected by odor, and by Drager tube measurement. The greatest source of solvent vapor was during the wipedown of plates. After washing, the plates were set on top of the tank, and a perchloroethylene soaked rag was used to wipe off excess monomer residue.

Drager tube measurements during this operation and some time after showed perchloroethylene vapor concentrations between 100-125 ppm (table II). The solvent wipedown is done for every plate that is washed. No local ventilation above the washtank is provided for this operation.

Another potential health problem caused by the plate washing tank may be contact dermatitis caused by skin contact with unreacted monomer, possibly acrylates, from old solvent residue. The worker is exposed when he pulls the plug to drain old solvent and residue, and when he replugs the tank to put in new solvent.

Chlorine fixing solution was used on only one plate during the NIOSH investigation. No detectable levels were found by Drager tube. Workers complained that on days when chlorine is used more frequently it is very irritating to the eyes, nose, and throat. NIOSH investigators observed that when chlorine solution was wiped on to the plate, chlorine gas from the solution was pulled through the workers breathing zone toward the exhaust grill (figure 1). Smoke tube measurements confirmed this observation.

B. Medical

NIOSH medical questionnaires were handed out to both photopolymerization plate workers and were filled out during their breaks. Only one of the two employees mentioned that he had health problems which could be related to work. The worker said that his nose was plugged most of the time, and his throat was irritated easily. He reported these symptoms started after using the iodine process and that his symptoms were caused by iodine and chlorine exposure. The other worker had no complaints and did not report any other health problems. Neither worker smokes. The first worker was interviewed by a NIOSH industrial hygienist based on his questionnaire responses. During the interview the worker elaborated about his respiratory symptoms and also reported a rash on his left forearm. This rash, he felt, was caused by the perchloroethylene solution in the platewashing tank. The rash may be caused by the worker dipping his arm into the tank and pulling the solvent plug. NIOSH industrial hygienists believe that skin contact with the unreacted monomer in solution (acrylates), may be the agent causing the workers rash.

C. Recommendations

These recommendations are presented to guide the employer in providing safe and healthful working conditions for the workers.

1. Engineering Controls

   a. Provide local exhaust ventilation for those operations which cause or allow solvents, chlorine gas, or iodine vapor, to be emitted into the workers breathing zone.

   b. Improve the local exhaust system in the platewashing tank to insure that solvent vapors are adequately captured when the tank lid is opened.

   c. Provide local exhaust above the platewashing tank so that vapors from solvent soaked rags are adequately removed during plate wipedown.

   d. Make sure that the wall exhaust in the photopolymer plate pro cessing room is always on.

   e. Install a non-corroding stem to the plug in the platewashing tank. This will eliminate any unnessary skin contact with solvents and acrylate residue.

   f. The plotopolymer plate processing room is overcrowded with machines and high production demands. This room should be re designed and expanded to accommodate present and future production needs.

   g. The Ohio State Department of Health has submitted ventilation guidelines to the Container Graphics Company for their review and implementation. NIOSH has not reviewed these guidelines, but does encourage expedious review and engagement of ventilation controls that will decrease atmospheric contaminents to their lowest possible levels.

2. Solvent Handling

   a. Continue the use of aprons and solvent-resistant gloves when handling solvents, chlorine solution, and iodine solution.

   b. Properly dispose of used solvent rags, Those solvent rags still in use should be stored in cans with properly sealing lids to contain solvent vapors.

3. Personal Protection

   a. Use of the Wilson half-face respirator (R635) and Wilson cartridge (R25) is NIOSH-approved for organic vapor and acid gas contaminants However, respirators are a last resort toward controlling contaminants in the workers breathing zone and

should only be used under temporary conditions. Therefore, until proper ventilation controls are installed workers should:

1. Get medical approval to wear respirators.
2. Be fit-tested for proper respirator size.
3. Change chemical cartridges in the respirator every two weeks (based on our estimated exposure).
4. Be instructed on the proper maintenance and storage of respirators.
5. Not be allowed to have a full beard since a good respirator-face seal is often not possible with facial hair.
6. Store respirators and cartridges in another room to avoid inadvertent organic vapor contamination.
7. Make sure that respirators are NIOSH certified.

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TABLE I

Results of Air Sampling for Iodine
Personal and Area Samples
Container Graphics Corporation

Time (hours/minutes)	Sampled Volume (Liters)	Location	Results Iodine (I_2) Vapor (PPM) [A]
7 hr 25 min	267	Personal sample, plate maker plate making room	> .002
6 hr 45 min	237	Personal sample, plate maker plate making room	> .005
7 hr 3 min	245	Personal sample, NIOSH observer	non-detectable
7 hr 55 min	279	General area, inside iodine curtain	.012
7 hr 50 min	274	General area, outside iodine curtain	non-detectable
7 hr 55 min	274	General area, chlorine iodine window	.005
7 hr 40 min	259	General area, over oven	non-detectable
7 hr 25 min	214	General area, photopolymer doorway exit	non-detectable
0 hr 21 min	21	General area, above iodine tank	> .05
0 hr 21 min	21	Personal, iodine application cycle (plate immersion, wash, drying)	.05
0 hr 18 min	18	General area, above drying oven	non-detectable
0 hr 20 min	20	Personal, iodine application cycle	.12
0 hr 20 min	20	General area, above iodine tank during application cycle	.15

Environmental Criteria

NIOSH[B]	——
ACGIH	0.1[C]
OSHA	0.1

A Parts of I_2 per million parts of air.
B NIOSH had not developed any environmental criteria for iodine vapor at this writing.
C The ceiling value for Iodine Vapor is 0.1 ppm, which should not be exceeded at any time.

TABLE II

Results of Drager Tube Air Sampling
for
Perchloroethylene and Chlorine

Time	Solvent	Location	Operation	Level in ppm*
10:30 a.m.	Perchloroethylene	Breathing zone above plate washing tank	Plates being taken from plate washer and put into drying oven	125
10:35 a.m.	Perchloroethylene	Above recirculating solvent storage tanks	Specific gravity check	N.D.**
2:15 p.m.	Perchloroethylene	Middle of plate proc-cessing room 1	All machine lids closed	100
2:25 p.m.	Perchloroethylene	Middle of plate proc-cessing room 1	Perchloroethylene wiping of plates after removal from tank	125
2:30 p.m.	Chlorine	Breathing zone above wash tank	Chlorine fixing of cryel plate	N.D.
2:35 p.m.	Perchloroethylene	Middle of plate proc-cessing room 1	All machine lids closed	100

Environmental Criteria:	Perchloroethylene	Chlorine
NIOSH	50[A] (100)[B]	0.5[B]
ACGIH	100	1.0
OSHA	100 (200)[B]	1.0

*Parts of contaminant per million parts of air
**N.D. = non detectable
A As an 8-hour timeweighted average concentration
B Ceiling value - contaminant not to exceed this value. Fifteen minutes allowed for maximum allowable level.

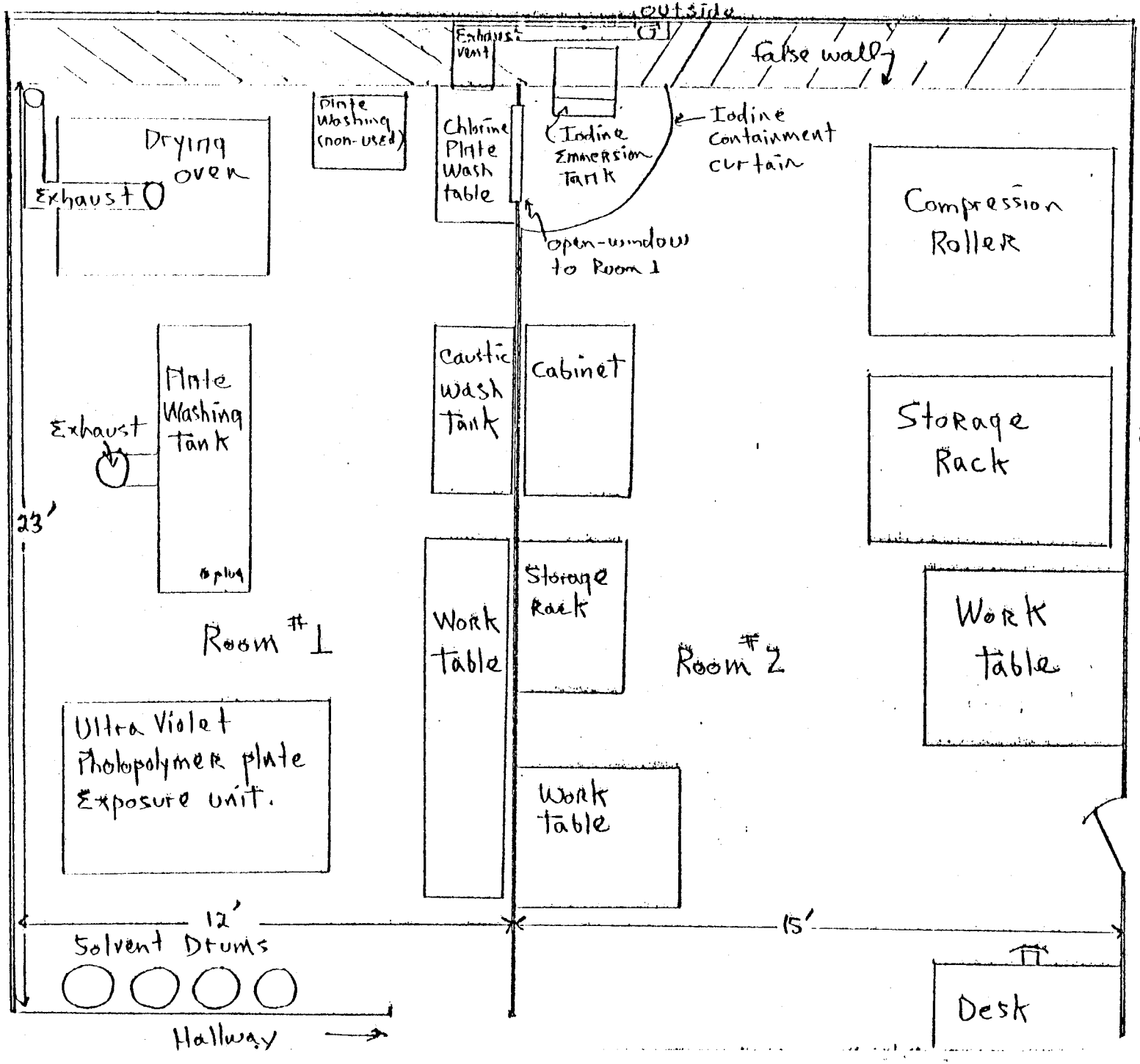

FIGURE 1
Container Graphics Corporation
Photopolymer Plate Processing Rooms
Toledo, Ohio