Health Hazard Evaluation Report

HETA 83-458-1800 TROPICANA PRODUCTS BRADENTON, FLORIDA

#### II. INTRODUCTION

Reports of dermatitis and respiratory problems among workers in a citrus juice bottling operation involving the use of UV-cured printing inks, prompted a request for a NIOSH health hazard evaluation on September 16, 1983. The request was submitted by the Senior Vice President for Technical Services, Tropicana Products Inc., Bradenton, Florida. On September 23, 1983, a similar request was also sent to NIOSH from an industrial hygienist with the International Brotherhood of Teamsters, Washington, D.C.

On November 2, 1983, an initial survey was conducted at the plant. Skin examinations and confidential interviews were conducted by a NIOSH medical officer during a follow-up survey on February 13, 1984. An extensive environmental and medical investigation was performed December 14-23, 1984. Preliminary findings and recommendations were provided by NIOSH in letters sent December 13, 1983 and April 10, 1984. The results from the environmental investigation were issued to company and union representatives as an interim report on March 25, 1985, followed by an interim report of the medical findings on August 28, 1985.

#### III. BACKGROUND

The Tropicana citrus processing plant in Bradenton, Florida is the largest citrus processor in the world. Opened in 1949, the plant processes 18% of all the citrus produced in the United States. The 280 acre facility employes 2700 people and includes 3 glass plants, a carton plant, and a plastics plant. Tropicana produces about 1.6 million gallons of orange juice and 2 million gallons of other juice beverages each week.

Workers in the "Vac-Pac" area of the Glass Filling Department had complained of dermatitis and possible respiratory problems from exposures to a special ultraviolet (UV) cured ink used in printing the Tropicana logo on 7oz., quart, and half-gallon glass bottles. Because of the high-speed filling operation, a fast-cure ink was required. This ink was applied to the side of the bottle using a screenprinting method, and cured with ultraviolet light just before the bottles were washed, sterilized, and filled. Silkscreen printing machines were located on 6 (lines 10-15) of 9 fill lines. Two lines for each of the three bottle sizes were available. The three remaining lines (16-18) filled 10 oz. bottles using paper labels. Lines 10, 12, and 13 also had paper label machines. During and after the NIOSH investigation Tropicana was phasing out the screenprinting operations and was installing paper label equipment on all fill lines.

#### A. Bottle Filling Process

Cardboard cases of empty bottles were fed by roller conveyers leading to the fill line where bottles were pulled through the line on a series of stainless steel conveyer belts. The cartons were lifted from the bottles which entered single file into a washer tunnel. Next, the side of the bottles being printed was sprayed with a methanol/water solution containing organo-silane coupling agents. This pre-spray, which insures proper adhesion of the ink to the glass surface, was automatically applied as the bottles passed through an exhaust ventilated enclosure. The bottles then passed through a flame dryer on their way to the printing machine.

The ink decoration was applied as the bottles rode through this carousel-like machine which placed a small silkscreen mat at the side of the bottle and automatically squeegeed ink through the mat as the bottles rode once around. The bottles then passed through an exhaust-ventilated UV-curing oven. After curing, which took less than one second, the bottles were sprayed with a 10% hydrogen peroxide solution upon entering a long sterilizer tunnel leading to the fill machine. After filling, the bottles were capped, inspected, and recased.

Seven workers were needed to operate the line. Job assignments were: Lead Person, Relief Person, Decaser Operator, Printer Operator, Filler Operator, Caser Operator, and General Cleanup Worker. The Vac-Pac area operated three shifts per day, five days per week. Workers took a 10-minute break every two hours during the shift and had 20 minutes for lunch.

#### B. Printing Ink Usage

The UV cured ink, trade named Kolorcure, was specifically formulated for Tropicana by T&C Apex Printing Inks of Elk Grove Village, Illinois. The ink was a mixture of red and white pigments dispersed in an epoxy-acrylate oligomer (pre-polymer) which also contained trimethylolpropane triacrylate (TMPTA), a polyfunctional acrylic monomer. Other ink components were 2,2-dimethoxy-2-phenylacetophenone, a light-activated catalyst sold under the trade name Irgacure 651, and a hydrogen transfer agent (methyl diethanolamine), identified by T&C as Sensitizer #1. The ink was dispensed onto the squeegee applicators from nozzles which received ink under pressure through a series of hoses connected to a pressurized tank. Overflow ink was collected in pails placed on the floor under the printer machines. When full, the pails were carried to the ink storage room, where the ink was screened and prepared for re-use. One printer machine consumed about 5-10 gallons of ink each week.

Ink was delivered and poured into the printer machine tank by the printer mechanic, who was also responsible for picking up and returning the overflow pails to the ink storage room. The fill line workers with the greatest risk of incidental contact with UV-cured printing ink were the printer operators. At least twice daily, a printer operator had to change a worn out applicator. Wearing rubber gloves, the operator stopped the machine, removed the applicator and silkscreen, and rinsed off the excess ink with a wash solvent. The change-out procedure took 3-5 minutes. Worn applicators were later refurbished by the printer mechanic, but the silkscreens were discarded.

Following the initial investigation, the NIOSH industrial hygienist recommended that employees immediately remove printing ink from their skin with soap and water or other appropriate skin cleaners. Because soap and water were not available at the printer operators' work stations, the company furnished a waterless skin cleaner that easily removed uncured ink from the skin. This cleaner was a citrus-based product called Printers and Pressman's Citrus Hand Cleaner, manufactured by Vin-Dotco Inc, Largo, Florida. The skin cleaner was kept at the Printer Operator's work station to discourage the use of solvent for cleaning hands and skin.

#### C. Cleanup and Maintenance Activities

The most significant contact with ink and ink-contaminated wash solvent occurred on Fridays during the third shift, when printer operators washed down the entire printer machine with UVW 80 solvent. After the printer machines were washed down, the third- shift Relief Person emptied the pails of ink-contaminated wash solvent and the ink applicator/screen wash tanks into a 55-gallon drum for later disposal as a waste solvent. The printer operators and Relief Person wore rubber gloves and rubber rain suits when performing the third shift cleanup. The Relief Person also wore a face shield.

The ink wash solvent (UVW 80) used by the printer operators was a special solvent blend supplied by T&C. The maintenance department used a different solvent (Ashland #220 Thinner) to remove ink from the worn out applicators. The #220 thinner had been used by the printer operators before the NIOSH investigation, but because of the dermatitis outbreak early in 1983, Tropicana substituted the #220 thinner with UVW 80. After the outbreak, the company established a written policy requiring employees handling UV-cured inks to wear nitrile rubber gloves, a protective apron, and safety glasses. This policy also warned employees not to use solvent to wash ink from their skin.

Worn applicators were cleaned and refurbished by the printer mechanics on the second or third shift. The mechanic would pour about 2 gallons of #220 thinner into a 5-gallon bucket. Excess ink was blown from the applicator with an air nozzle, and the applicators were disassembled and placed in the bucket. Prior to the NIOSH investigation, the applicators were manually brushed clean by hand. After the initial reports of dermatitis, the printer mechanics devised an alternative cleaning method. By strapppng a vibrator to the bucket the wash slovent was sufficiently agitated to remove the ink without manual cleaning by the mechanic. The bucket was also covered to further reduce exposures when the applicators were being cleaned. After about a half-hour of agitation, the applicators were removed and refurbished by installing new rubber squeegees. A printer mechanic would typically clean and refurbish applicators about once every two weeks.

The chemical compositions of the solvents evaluated, as identified by the suppliers were:

#### UVW 80 Ink Wash Solvent

- -- 50-90% alkyl substituted benzenes (i.e. methylbenzene)
- -- 10-50% 2-butoxyethanol (butyl cellosolve)

#### Ashland #220 Thinner

- -- 10-30% toluene
- -- 30-60% acetone
- -- 10-30% mineral spirits
- -- 10-30% isopropyl alcohol
- -- 1-10% ethylbenzene

One other chemical used in the Vac-Pac area that could also cause dermatitis was Sterilex, a quanternary ammonia compound used to sterilize the juice filler machines. This chemical was labeled as a "corrosive, which can cause skin and eye damage." Sterilization was required after any maintenance work was performed on the filler equipment or filler machine housing. Sterilex was drawn from a tap inside the filler housing. Vac-Pac workers estimated that Sterilex was used about once a week.

#### IV. EVALUATION DESIGN AND METHODS

#### A. Initial Survey (November 1983)

NIOSH investigators conducted a walk-through survey in the Vac-Pac Department to observe juice bottling operations and employee work practices. The NIOSH industrial hygiene investigator directed specific attention toward those operations involving exposures to inks and other chemicals. A list of the chemicals and solvents used on the bottling

lines was compiled. From two of the bottling lines, bulk air samples were collected on activated charcoal tubes placed inside the UVW-80 wash solvent tanks. A small sample of the liquid solvent was also collected. The samples were later analyzed in the NIOSH laboratory using a gas chromatograph/mass spectrometer (GC/MS) to identify the volatile organic compounds contained in, or released from, the solvent. The formulation for the UV-cured printing ink was obtained from the supplier. NIOSH medical investigators conducted personal, confidential interviews with several of the 13 employees identified by union representatives as having suffered from skin rashes or other adverse health effects.

#### B. Employee Interviews (February 1984)

Based on the information and results obtained during the initial survey, NIOSH medical officers returned to the plant in February 1984 to conduct interviews and examine the skin of all 71 first— and second—shift employees in the Vac-Pac area, and a comparison group of 43 first shift workers from the Carton Filling Department. Carton filling workers had jobs similar to the Vac-Pac workers, but they were not exposed to UV-cured inks or solvents. Maintenance workers were not included in this survey because of their dissimilar exposure histories.

#### C. Follow-up Environmental/Medical Survey (December 1984)

A follow-up investigation was conducted by a NIOSH industrial hygienist and three NIOSH medical officers. They were assisted by a board-certified dermatologist from Tampa, contracted by NIOSH to perform the dermatological examinations and patch testing. During an initial meeting with company and union representatives, NIOSH investigators were told that skin problems had been greatly reduced by adherence to the work practices program outlined in the attached company memo (see Attachment A).

#### 1. Industrial Hygiene Survey

On December 13-14, 1984 an industrial hygiene survey in the Vac-Pac area was conducted to evaluate personal exposures to organic vapors for: (a) four 3rd shift Printer Operators and a Relief Operator who were cleaning printing machines with the UVW-80 ink wash solvent, and (b) a maintenance worker who was cleaning and refurbishing ink applicators with Ashland 220 thinner. The air samples were collected on charcoal tubes and analyzed by gas chromatography to quantify the organic vapors released from the solvents during use. The organic compounds sampled were selected based the results obtained from the GC/MS identification of volatile organics collected on fill lines 14 and 15 during the cleanup operation, or from the GC/MS analysis of a bulk liquid sample of Ashland 220 thinner.

Personal breathing zone samples were collected by attaching a charcoal tube holder to the worker's shirt collar. The charcoal tube holder was attached via a plastic tube to a battery-powered air sampling pump worn on the worker's belt. The air in the worker's breathing zone was sampled during the work tasks by pulling a known volume of air through the charcoal tube, which trapped the organic vapors present. The sampling pumps were pre-calibrated and set to a flow rate of 100 cc of air per minute. General area air samples were also collected in the solvent and ink storage rooms.

A bulk liquid sample of the UV printing ink was also analyzed to identify its organic components. Organic compounds were extracted from the ink sample using carbon disulfide. The extract was then analyzed by GC/MS. To better characterize unknown components found in the extract, the sample was also analyzed by gas chromatography- fourier transform infrared spectroscopy (GC-FTIR).

#### 2. Medical Survey

#### a. Interviews and Skin Examinations

On December 14-21, 1984, 47 Vac-Pac workers on the first and second shifts were interviewed and examined by NIOSH physicians and the dermatologist. Five Carton Filling workers and two workers from other departments, one of whom was a former Vac-Pac worker, were also interviewed and examined.

#### b. Patch Testing

To detect cases of skin sensitization (allergy), all the employees who were interviewed and examined were also patch tested to the components of the UV-cured ink and solvents. The substances tested were mixed in an appropriate inert vehicle such as petrolatum, in a concentration likely to be non-irritating to normal persons. A small amount of each mixture was then placed separately on the left side of the back and covered with a "patch" of non-absorbent material. Patches were fixed with non-irritating tape.

Page 8 - Hazard Evaluation and Technical Assistance Report No. 83-458

The components of the ink (supplied by the manufacturer) were mixed in petrolatum in appropriate non-irritating concentrations determined by reference to previous studies. The ink components and concentrations used were:

SUBSTANCE	CONCENTRATION			
Trimethylolpropane triacrylate	0.2%			
2,2-dimethoxy-2-phenylacetophenone	5.0%			
Methyl diethanolamine	0.0%			
Epoxy acrylate oligomer	1.0%			
Ashland 220 thinner	5.0%			
UVW-80 wash solvent	5.0%			
Thiuram	1.0%			
PPD Mix	1.0%			

The UVW-80 wash solvent and the 220 thinner were mixed in petrolatum at a 5% concentration. These concentrations were determined to be non-irritating by application to the skin of two NIOSH investigators. Two materials provided by the manufacturer, which were thought to be inert pigments, were applied full strength. Inert pigments are ordinarily non-irritating. However, because of a miscommunication, the ink formulator had provided "pigment concentrates" containing high concentrations of TMPTA as well as the inert pigment.

Two rubber mixtures (PPD mix and thiuram mix) from the standard tray of the American Academy of Dermatologists were applied in standard concentrations. All mixtures were applied to small cellulose discs with aluminum backing, and fixed to the left side of the back with non-irritating tape.

Patches were left on for 48 hours, the standard time period considered long enough for a reaction to develop in a previously sensitized person. Participants were instructed not to wash or to disturb the patches, and to avoid heavy exertion which could cause sweating. After 48 hours, patches were removed by the investigators and the area of each patch was numbered and marked. The participants' backs were examined again at 96 hours in order to note persistent or delayed reactions.

Reactions were scored according to a standard protocol. Positive reactions are scored as +1 (reddened, raised skin), +2 [reddened, raised skin with a few papules (pimple-like eruptions) or vesicles (small blisters)], or +3 (red, raised skin with ulcerations or small, closely set vesicles extending beyond the border of the patch). A +3 reaction is considered definitely indicative of allergic sensitization. A +1 reaction may only indicate irritation, especially if it does not persist to 96 hours.

#### c. Photo-patch Testing

Upon exposure to ultraviolet light, some substances may change to a form that makes them a more potent skin sensitizer. Since the substances used in the ink were exposed to UV light during the printing process, and since employees' skin received additional UV light from the Florida sun, controlled amounts of UV light were administered on areas where patch-test materials were applied.

The ink components and the solvents were applied to the right side of the back with occlusive patches in the same manner that the other patches were applied to the left side of the back. After 24 hours, participants were instructed to remove only the patches on the right side of the back to expose the skin to 1/2 to 1 hour of full sunlight. The ordinary patches, on the left side of the back, were left undisturbed, and participants were instructed to cover them with an additional opaque material during sunlight exposure. Participants were instructed not to wash the right side of the back until the examinations at 48 hours and 96 hours had taken place. Photo-patch reactions were scored the same way as the ordinary patches. A person was considered to have a photo-allergy to a substance only if they reacted to the substance on the photo- patch test but did not react to the same substance on the ordinary patch test.

#### V. EVALUATION CRITERIA

#### A. Environmental Criteria

As a guide to the evaluation of the hazards posed by workplace exposures, NIOSH field staff use 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. However, 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 pre-existing medical condition, 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 are often not considered in the evaluation criteria. Also, some substances are absorbed by direct contact with the skin and mucous membranes which could potentially increase the total exposure. Lastly, 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), 1 and (3) the U.S. Department of Labor (OSHA) occupational safety and health standards. 2 Often, the NIOSH recommendations and ACGIH TLVs 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. The OSHA standards also may be required to take into account the feasibility of controlling exposures in various industries where the agents are used; the NIOSH-recommended exposure limits, by contrast, are based primarily on concerns relating to the prevention of occupational disease. When considering the exposure levels and the recommendations for reducing these levels found in this report, employers should note they are legally required to meet those levels specified by an OSHA standard.

For those compounds with established occupational exposure limits, the various criteria proposed by OSHA, ACGIH, and NIOSH for airborne concentrations of the chemical substances measured in this evaluation are listed below. A time-weighted average (TWA) exposure refers to the average airborne concentration of a substance during a normal 8 to 10-hour workday. Some substances have recommended short-term exposure limits (STEL) or ceiling (C) values which are intended to supplement the TWA where there are recognized toxic effects from high short-term exposures.

The environmental evaluation criteria and major health effects associated with the substances monitored as part of this study are presented below.

#### RECOMMENDED EXPOSURE LIMITS

SUBSTANCE	8-10 HOUR TWA	SOURCE	HEALTH EFFECTS
Toluene	100 ppm	NIOSH	central nervous system
	100 ppm	ACGIH	depressant <sup>3</sup>
	200 ppm	OSHA	
Xylene	100 ppm	NIOSH	central nervous system
	100 ppm	ACGIH	depressant, respiratory
	100 ppm	OSHA	irritation <sup>3</sup>
Acetone	250 ppm	NIOSH	irritation; liver, kidney,
	750 ppm	ACGIH	and nervous system effects3
	1000 ppm	OSHA	2

Page 11 - Hazard Evaluation and Technical Assistance Report No. 83-458

SUBSTANCE	8-10 HOUR TWA	SOURCE	HEALTH EFFECTS
Isopropanol	400 ppm	NIOSH	mucous membrane irritation <sup>3</sup>
	400 ppm	ACGIH	
	400 ppm	OSHA	
Total alkanes	500 ppm	NIOSH	skin and nervous system
(as n-heptane)	400 ppm	ACGIH	effects <sup>3</sup>
	500 ppm	OSHA	
Butyl Cellosolve	LEP*	NIOSH	eye and upper respiratory
(2-butoxyethanol)	25 ppm	ACGIH	irritation, possible
ĭ	50.ppm	OSHA	reproductive effects4,5
Aromatic hydrocarbons		NIOSH	skin and mucous membrane
(as trimethylbenzene)		ACGIH	irritation, possible nervous
		OSHA	system effects,
asthmatic			bronchitis4

\* LEP = lowest extent possible

#### B. Toxicology

#### 1. Solvents

The solvent components evaluated for this survey (toluene, xylene, acetone, isopropanol, alkanes, aromatics, and 2-butoxyethanol) are primarily absorbed by inhalation or through the skin in workplace exposures. Excessive exposure to solvents may result in neurologic effects and dermatological effects, including eye and upper respiratory tract irritation, sleepiness, fatigue, headache, memory disturbance, difficulty in concentrating, nausea, vomiting, abdominal cramps, loss of appetite, weight loss, flushed skin, skin defatting and irritation, and folliculitis (inflammation of hair follicles). The intoxicating effects of alcohol are frequently increased when alcoholic beverages are consumed after exposure to solvents.6,7,8,9

Extreme exposures may result in tremor, loss of coordination, mental confusion, loss of consciousness, coma and death. In addition, excessive or prolonged exposure to some of these solvents may result in chronic or delayed-onset effects including visual disturbances, loss of the sense of smell and touch, impaired coordination, decreased nerve conduction velocity, neurobehavioral changes, and kidney and liver damage.

#### 2. Butyl Cellosolve (2-butoxyethanol)

Exposure of humans to high concentrations of 2-butoxyethanol (2-BE) vapors from 300-600 ppm for several hours would be expected to cause respiratory and eye irritation, narcosis, and damage to the kidney and liver. Butoxyethanol is metabolized, at least in part, to butoxyacetic acid and this substance is excreted in the urine of exposed animals and human subjects. <sup>10</sup> It penetrates the skin readily and toxic action from excessive skin exposure may be more likely than from vapor inhalation. <sup>4</sup>

Both 2-BE and butoxyacetic acid increase osmotic fragility of the red blood cells, an effect most pronounced in rodents even at concentrations as low as 50 ppm. From industrial experience and short term exposures of human volunteers, it has been suggested that humans are less susceptible to induced hemolytic anemia from exposure to 2-BE. Although the rat appears more susceptible than other animals and humans in this respect, anemia is not an uncommon condition in the human population. Therefore, the ACGIH has recommended that exposures be maintained below levels which have been found to cause blood changes in experimental animals, with 25 ppm being the most practical "no ill effect" level.<sup>4</sup>

Butyl cellosolve is part of a family of glycol ethers. Recently, exposure studies with laboratory animals have shown significant toxicological effects on reproduction from several commonly used glycol ethers. Several recent studies have demonstrated dose-related embryotoxicity and other reproductive effects in several species of animals exposed by different routes of administration. Of particular concern are those studies in which exposure of pregnant animals to concentrations of 2-methoxyethanol (2-ME) and 2-ethoxyethanol (2-EE) at or below their respective OSHA PEL led to increased incidences of embryonic death, teratogenesis, or growth retardation. Exposure of male animals resulted in testicular atrophy and sterility. 11 Preliminary test results of some structurally related glycol ethers, including 2-BE, indicate that they also have the potential for causing adverse reproductive effects similar to 2-ME and 2-EE.4 In light of these findings, NIOSH recommends reducing exposures to the lowest extent possible for these structurally related glycol ethers until adequate testing demonstrates their safety. 11

#### 3. Aromatic Hydrocarbons

Aromatic hydrocarbons are primary skin irritants, and repeated or prolonged skin contact may cause dermatitis because of their dehydrating and defatting properties. Direct contact to the eye from aromatic liquids may cause burns, lacrimation, and irritation. Conjunctivitis and corneal burns have been reported from the  $\rm C_6-\rm C_8$  aromatics.  $^{12}$ 

As previously noted, the NIOSH laboratory found the aromatic hydrocarbon components in the solvents used in the Vac-Pac area were mostly  $C_9$ - $C_{10}$  alkyl substituted benzenes. The evaluation criteria selected for quantitating exposures to these compounds was 1,2,3-trimethylbenzene. Trimethylbenzenes are frequently used as solvents, and as motor fuel components.  $^{12}$  According the ACGIH, the only published report of human exposures to these compounds found workers had developed symptoms of nervousness, tension, and anxiety, and asthmatic bronchitis. In this study exposures ranged from 10 to 60 ppm. On the basis of this study the ACGIH has recommended a TLV of 25 ppm as an 8-hour TWA for trimethylbenzene and its structurally related isomers.  $^4$ 

#### 4. Ultraviolet Cured Printing Inks

The main ingredients of the UV-cured ink were:

- Epoxy-acrylate oligomer (a prepolymer and the major component)
- Trimethylol propane triacrylate (a polyfunctional acrylic monomer)
- 2,2-dimethoxy-2-phenylacetophenone (light activated catalyst)
- 4. Methyl diethanolamine (hydrogen transfer agent)
- 5. Red and white pigments

Allergic contact dermatitis has been associated with epoxy-acrylate oligomers and TMPTA. 13,14 Previous studies have not shown any of the ink components to be photo-toxic.

#### VI. EVALUATION RESULTS AND DISCUSSION

#### A. Environmental

The GC/MS analysis of the 220 thinner liquid identified toluene, xylenes, various  $C_6$ - $C_8$  alkanes, acetone, and isopropanol (see Figure 1). Although this solvent had been used to clean machines and equipment on the fill lines before the NIOSH evaluation was requested, only the maintenance personnel were still using 220 thinner. Its use was limited to cleaning ink applicators in the ink storage room. This room was located near a loading dock on the floor below the Vac-Pac area. Since the maintenance mechanics no longer cleaned ink applicators with a brush over an open pan of solvent, exposures to airborne solvent vapors were well controlled. The air sampling results for the personal and two area samples collected during the cleaning of ink applicators are shown in the first section of Table 1.

The second section of Table 1 shows the monitoring results for solvent vapor exposures during the third shift cleanup of the Vac- Pac printing machines with UVW-80 wash solvent. The organic vapors sampled were those identified in a GC/MS analysis of two air samples collected near where printer operators were washing down their machines with UVW-80 solvent. The GC/MS analysis (see Figure 2) mostly detected a variety of alkyl substituted benzenes such as propyl benzenes, trimethylbenzenes, and methylethyl-benzenes. Also detected were xylenes, and butyl cellosolve (2-butoxyethanol). Personal exposures to these organic vapors were measured from quantitative analysis of additional air samples. The sampling results found that the exposures were mostly to aromatic hydrocarbons ranging in concentrations from 6.5 to 57.3 ppm.

Using the ACGIH TLV of 25 ppm for trimethylbenzene as the evaluation criteria, three of the five printer operators sampled were excessively exposed to airborne aromatic hydrocarbons during the weekly cleanup of the printing machines with UVW-80 wash solvent. Also, when the potential for adverse reproductive effects from glycol ethers are considered, the personal exposures detected for butyl cellosolve (up to 10 ppm) may also be excessive.

GC/MS analysis of the ink extract was not successful. Although the analysis found several components, none of them were positively identified by GC/MS. Re-analysis by GC-FTIR indicated that most of these compounds were possibly esters such as alkyl acrylic acid esters. None of these types of compounds were detected on any of the air samples collected.

#### B. Medical

#### 1. Initial Medical Survey

Only 3 (6%) of the 47 Vac-Pac workers interviewed reported a rash not attributable to other causes in the past 9 months; the workers associated these rashes with specific spills of ink or solvent onto clothing. The percentage of ink- and solvent-exposed workers (printers and relief operators) who stated they used gloves "most of the time" had actually decreased significantly since February 1984, but general hygiene, such as immediate cleaning of contaminated skin, had reportedly improved.

Examination revealed numerous cuts on the arms and hands of 20 of 47 Vac-Pac employees. Similar findings were noted in the February 1984 examinations and were attributed to broken glass and sharp machine parts. No skin rashes, not attributable to other causes such as fungal

infections, were found on examination. The third shift printer operators, who in retrospect, probably had the highest potential for skin contact with solvents and inks during the weekly cleanup of the fill lines, were not included in the medical survey

Although preliminary results from the initial interviews suggested an association between work in the Vac-Pac area and skin rashes, NIOSH investigators could not determine if the skin reactions were allergic or irritant dermatitis, or which chemical exposures were associated with skin reactions.

#### 2. Patch Testing

Two persons (4%) of the 47 participants had +3 reactions to TMPTA; one to the ordinary patch, and one to both the photo-patch and the ordinary patch; at 48 and 96 hours (table 2). Another had a +2 reaction to methyldiethanolamine on the ordinary patch at 48 hours only. A fourth person had a +3 reaction to thiuram mix at 96 hours, and a fifth person had a +3 reaction to the PPD mix at 48 and 96 hours.

Mild +1 reactions to the methyldiethanolamine were found on ordinary patch-testing in an additional eight persons (17%): four at 48 hours only, two at 48 hours and 96 hours, and two at 96 hours only. Four (9%) had a +1 reaction to the UVW 80 solvent (all at 48 and 96 hours). Four (9%) persons had a +1 reaction to the 220 thinner (one at 48 hours and three at 48 hours and 96 hours). An additional three (6%) reacted mildly (+1) to TMPTA (all at 48 and 96 hours). All persons with these reactions were either current or former employees in the Vac-Pac area.

All employees participating in the patch testing, no matter where they worked, had definite irritant reactions to the pigment concentrate patches, which inadvertently contained high concentrations of TMPTA. (Employees with skin peeling or blistering were given hydrocortisone cream to apply to the affected areas, and were offered free follow-up visits or telephone consultations with the consultant dermatologist. No subsequent difficulties have been reported).

#### VII. DISCUSSION AND CONCLUSIONS

Third shift Vac-Pac workers who were cleaning printing machines with UVW-80 wash solvent were overexposed to aromatic hydrocarbons. Exposures were well below the evaluation criteria for the other ingredients of the solvents used. No inhalation hazard was detected from the ink itself. With implementation of new work practices for cleaning and refurbishing ink applicators, mechanics experienced only minor inhalation exposures to 220 thinner vapors.

That the TMPTA in the ink is a sensitizer has been shown in many other studies and is confirmed in this one; two employees had definite allergic reactions to it. Furthermore, the allergic reactions to TMPTA demonstrated in this and in other studies were to TMPTA alone. The +2 reaction to methyldiethanol-amine was likely to have been a false positive reaction, since it was not still visible at 96 hours. The employee who reacted to the thiuram mix may have been allergic to components of the nitrile gloves provided by the company. The employee who reacted to PPD mix, which is a mixture of the components of "black" rubber, would probably have no reaction to the rubber gloves. No conclusions about allergic sensitization should be drawn from the reactions to the pigment concentrates, since the concentrations of TMPTA contained in them were inappropriately high for patch testing.

The other positive reactions are less easy to interpret, since they were less strong. Some of those with a +1 reaction to TMPTA may have been genuinely sensitized, especially those who had the reaction at 96 hours; others may have been showing an irritant reaction. Epoxy acrylate oligomers have been shown in other studies to be sensitizers, but no allergic reactions were found here. Neither the solvents, nor the other components of the inks, have been definitely shown by this study (or other studies) to cause allergic reactions.

TMPTA is a known skin irritant and skin sensitizer. Several other components of the ink and solvents evaluated are also irritants. Since few employees tested showed sensitization to TMPTA or the other chemicals evaluated, the NIOSH investigators concluded that past skin reactions reported among the Tropicana Vac-Pac workers were irritant, but not allergic, reactions to components of the ink or solvent. Consistent with other investigations, photo-toxic reactions to the ink components or solvents were not demonstrated in any of the study participants. Before the practice was prohibited by company policy, the use of solvents to remove ink from the skin or clothing may have caused more widespread irritation than actual skin contamination from the ink itself.

The wearing of protective gloves, most often considered a solution to the problem of skin contact with chemicals, may actually have contributed to the skin irritation problems if chemicals were allowed to get inside the gloves, or if the gloves were not changed frequently. Some of the solvent components, including toluene, xylene, and acetone, can permeate nitrile rubber gloves in less than 90 minutes. <sup>15</sup> At least two workers tested in this study reacted to rubber components, and may have been allergic to the gloves themselves. Using protective gloves most likely did not account for the decrease in reported skin problems at the time of the follow-up survey, since many workers reported that glove use had decreased after

the initial NIOSH visit. The providing of waterless skin cleaner at the work stations, and the new method for cleaning ink applicators, were more likely responsible for controlling dermatitis.

#### VIII. RECOMMENDATIONS

The following recommendations were made in previous reports and are repeated here. However, since our survey was conducted, Tropicana has stopped using UV-cured printing inks. Tropicana now uses paper labels on all glass beverage containers.

- An ink wash solvent with a lower percentage of aromatic hydrocarbons should be found for the weekly wash-down of printing machines during third shift. Otherwise, ventilation to the Vac-Pac area should be increased or NIOSH-approved organic vapor respirators should be worn.
- 2. Emphasis on good hygiene, and the provision of skin cleansers at the work stations, should be continued. Gloves should be worn for protection only if they are changed often. Gloves should not be cleaned with solvent. Contaminated gloves should be changed immediately. An irritating chemical held against the skin inside contaminated gloves may cause a more severe skin reaction than the same chemical on open skin.
- 3. Disposable protective clothing should be provided for workers on the third shift who must break down and clean the printing machines each week. The heat stress placed on workers wearing the rubber rain suits discourages the workers from wearing the suits. The necessity of cleaning the suits (or the alternative, the re-wearing of contaminated suits) provides a good opportunity for exposure to inks and solvents.
- 4. Opportunities for exposure to broken glass and sharp machine parts should be reduced.

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#### XI. DISTRIBUTION AND AVAILABILITY

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Copies of this report have been sent to:

- 1. Tropicana Products Inc.
- 2. International Brotherhood of Teamsters
- 3. International Brotherhood of Teamsters, Local 173
- 4. NIOSH Regional Office, Atlanta, Georgia
- 5. U.S. Department of Labor, OSHA, Region IV

For the purpose of informing affected employees, copies of this report shall be posted by the employer in a prominent place accessible to the employees for a period of 30 calendar days.

# HETA 83-458 TROPICANA PRODUCTS, INC. BRADENTON, FLORIDA SOLVENT THINNER USED BY MAINTENANCE

Total

December 13, 1984

Job Classification	Sample No.	Start Stop	minutes	Sample Vol liters	Toluene ppm	Xylene ppm	Acetone ppm	Isopropanol ppm	Alkanes ppm**
220 Thinner Usage	T1	1620 2000	210	21.42	2.00	0.46	r 22	2 21	2.46
2nd shift printer mech. Tl		1638 - 2008		21.42	3.98	0.46	5.33	3.31	3.46
Ink storage room Solvent storage room	T2 T3	1700 - 2010 1725 - 2012	190 167	21.32 17.15	3.29 2.54	0.30	2.32 0.30	2.40 1.50	2.11
Evaluation Criteria: ACGIH TLV NIOSH Recommended Sta	andard					100 ррт 100	750 ppm 250	400 ppm 400	400 ppm 440
OSHA PEL	ilidal d	*			200		1000	400	500
Job Classification	Sample No.	Start Sto	Decemb p minutes	Sample Vol liters	Butyl Cellosolve ppm	Toluene ppm	Xylene ppm	Other Aromatics ppm*	
2 7 23 9 27 2 7 722									
3rd Shift Ink Cleanup					0.00	-			~
Line 10 printer opr.	\$1	0019 - 022		12.48	9.75	0.12	2.33	57.30	
Line 10 printer opr. Line 13 printer opr.	S2	0023 - 033	5 192	8.60	1.73	ND	0.33	6.47	×
Line 10 printer opr. Line 13 printer opr. Line 15 printer opr.	S2 S3	0023 - 033 0052 - 030	5 192 8 136	8.60 13.52	1.73 6.36	ND ND	0.33	6.47 39.61	~
Line 10 printer opr. Line 13 printer opr.	S2 S3 S4	0023 - 033	5 192 8 136 5 164	8.60	1.73	ND	0.33	6.47	×
Line 10 printer opr. Line 13 printer opr. Line 15 printer opr. Line 14 printer opr. Relief opr. ink wash di	S2 S3 S4	0023 - 033 0052 - 030 0031 - 031	5 192 8 136 5 164	8.60 13.52 16.76	1.73 6.36 3.84	ND ND 0.26	0.33 1.41 1.30	6.47 39.61 31.62	×
Line 10 printer opr. Line 13 printer opr. Line 15 printer opr. Line 14 printer opr.	S2 S3 S4	0023 - 033 0052 - 030 0031 - 031	5 192 8 136 5 164	8.60 13.52 16.76	1.73 6.36 3.84	ND ND 0.26	0.33 1.41 1.30 0.85	6.47 39.61 31.62 19.41	· ·
Line 10 printer opr. Line 13 printer opr. Line 15 printer opr. Line 14 printer opr. Relief opr. ink wash dis	\$2 \$3 \$4 \$p \$7	0023 - 033 0052 - 030 0031 - 031	5 192 8 136 5 164	8.60 13.52 16.76	1.73 6.36 3.84 4.31	ND ND 0.26 0.27	0.33 1.41 1.30 0.85	6.47 39.61 31.62 19.41	

<sup>\*</sup> Other aromatics were mostly C 9 H 12 and C 10 H 14 alkyl substituted benzenes. The samples were quantitated using 1,2,3-trimethylbenzene as the standard.

\*\* Organic vapors detected were mostly C 6 -C 8 alkanes. N-heptane was used to quantitate the samples.

# TABLE 2 HETA 83-458 TROPICANA PRODUCTS, INC. BRADENTON, FLORIDA

## POSITIVE PATCH TEST RESULTS FOUND AMONG PARTICIPANTS CURRENTLY OR FORMERLY WORKING IN THE VAC-PAC AREA

December 14-21, 1987

SUBSTANCE		TIME OF READING AND REACTION 48 hours 96 hours						
more.	CONCT	(+3)	(+2)	(+1)	(+3)	(+2)	(+1)	
Trimethylolpropane triacrylate	0.2%	2	0	3	2	0	3	
2,2-dimethoxy-2-phenylacetophenone	5.0%	0	0	0	0	0	0	
Methyl diethanolamine	0.0%	0	1	6	0	0	4	
Epoxy acrylate oligomer	1.0%	0	0	0.	0	0	0	
Ashland 220 thinner	5.0%	0	0	4	0	0	4	
UVW-80 wash solvent	5.0%	0	0	4	0	0	3	
Thiuram	1.0%	1	0	0	1	0	0	
PPD Mix	1.0%	1	0	0	1	0	0	

<sup>+3</sup> Reaction = red, raised skin with ulcerations or small closely set vesicles extending beyond the border of the patch

<sup>+2</sup> Reaction = reddened, raised skin with ulcerations or small blisters

<sup>+1</sup> Reaction = reddened, raised skin

FIGURE 1
HETA 83-458
TROPICANA PRODUCTS, INC.
BRADENTON, FLORIDA

GC/MS RESULTS - ASHLAND 220 THINNER

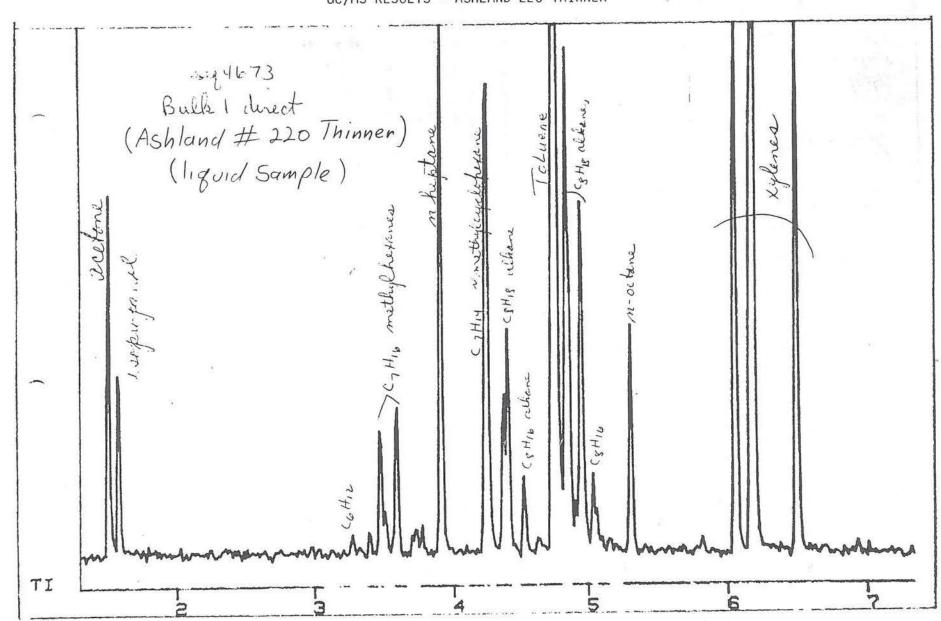
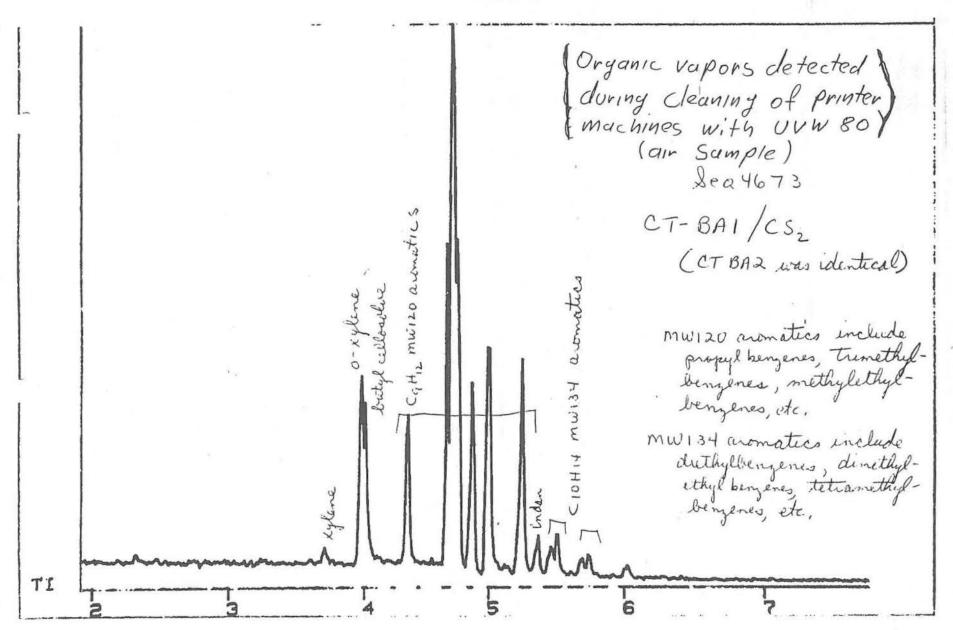


FIGURE 2
HETA 83-458
TROPICANA PRODUCTS, INC.
BRADENTON, FLORIDA

GC/MS RESULTS - UVW 80 WASH SOLVENT



#### ATTACHMENT A. (to NIOSH HETA Report 83-458)

### PROCEDURES TO BE FOLLOWED TO INSURE THE SAFE HANDLING AND USE OF U.V. INK IN GLASS FILLING

- U.V. inks and U.V. ink solvents can cause eye and skin irritation. AVOID DIRECT CONTACT WITH SKIN!
- The following protective equipment must be worn when handling U.V. ink and during cleaning operations:
  - a. Long rubber "Sol Vex" gloves
  - b. Safety glasses
  - c. Rubber or vinyl protective aprons
  - d. Barrier cream (optional)
- When U.V. inks are spilled on clothing, the affected items must be removed as soon as possible. Ink residues must be removed from clothing by detergent washing before reuse.
- 4. Rings, wrist watches and bracelets must not be worn, since ink can become trapped under them, giving risk to prolonged ink-to-skin contact.
- 5. Employees must wash with soap and water before eating to avoid the possibility of U.V. ink ingestion.
- 6. Smoking will not be permitted at any time on or near U.V. ink products and solvents or associated production equipment.
- 7. All U.V. ink spills should be scraped up, then wiped clean with rags.
- 8. U.V. Ink First Aid Procedures:
  - a. In case of skin contact, wash affected skin area with soap and water, not solvent.
  - b. In case of eye contact, flush the eye area with copious amounts of cool water for about 15 minutes. Report to the Nurse.
  - c. In case of ingestion, induce vomiting and report to the Nurse immediately.
- 9. All U.V. ink pails must remain covered at all times.
- All U.V. ink pails should be disposed of as soon as they have been emptied.
- 11. The U.V. ink screen wash solvent in the screen wash tanks must be emptied and replaced with new solvent once a week. It is important that all old solvent is emptied into the proper receptacle.
- 12. Printer operators, on start-up, should check to be sure the screen wash tanks contain clean solvent.

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