

U. S. DEPARTMENT OF HEALTH, EDUCATION AND WELFARE
CENTER FOR DISEASE CONTROL
NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH
CINCINNATI, OHIO 45226

HEALTH HAZARD EVALUATION DETERMINATION REPORT
HE 77-70-515

ROCK HILL PRINTING & FINISHING COMPANY
ROCK HILL, SOUTH CAROLINA

AUGUST 1978

I. TOXICITY DETERMINATION

The National Institute for Occupational Safety and Health (NIOSH) conducted a combined environmental-medical evaluation on January 25 - 27, 1978 for employees of the Screen Print Preparation Department of the Rock Hill Printing and Finishing Company. Employee exposure to the following airborne contaminants was evaluated: benzene, xylene, decane, undecane, azo dyes, diazonium salts, formaldehyde, phenol, phosphine, sulfur dioxide and methanol. It has been determined that during the period of this evaluation, occupational exposure to airborne concentrations of the aforementioned chemical contaminants did not constitute a health hazard. This determination is based on environmental measurements of airborne contaminants, confidential employee interviews, observations of work practices and engineering controls, and a review of the relevant literature.

II. DISTRIBUTION AND AVAILABILITY OF DETERMINATION REPORT

Copies of this Determination Report are currently available upon request from NIOSH, Division of Technical Services, Information and Dissemination Section, 4676 Columbia Parkway, Cincinnati, Ohio 45226. After 90 days the report will be available through the National Technical Information Service (NTIS), Springfield, Virginia. Information regarding its availability through NTIS can be obtained from NIOSH, Publications Office at the Cincinnati address.

Copies of this report have been sent to:

1. Director, Safety, Medical & Plant Protection -
Rock Hill Printing and Finishing Company
2. President - Textile Workers Union of America
Local 710
3. Director Occupational Safety and Health -
Amalgamated Clothing and Textile Workers Union

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4. U. S. Department of Labor - Region IV

5. NIOSH - Region IV

For the purpose of informing the 9 potentially exposed employees, the employer shall promptly "post" for a period of 30 calendar days the Determination Report in a prominent place(s) near where the affected employees work.

III. INTRODUCTION

Section 20 (a)(6) of the Occupational Safety and Health Act of 1970, 29 U.S.C. 669 (a)(6), authorizes the Secretary of Health, Education, and Welfare; following a written request by any employer or authorized representative of employees, to determine whether any substance normally found in the place of employment has potentially toxic effects in such concentrations as used or found.

The National Institute for Occupational Safety and Health received such a request from nine employees of the Screen Print Preparation Department of the Rock Hill Printing and Finishing Company, requesting that NIOSH evaluate airborne emissions from the dyeing of polyester fabric. The employees indicated that the chemical "fumes" generated during the dyeing process could be detected by taste and produced the following subjective symptoms: headache, and irritation of the eyes, nose, and throat. The employees were concerned that prolonged exposure to this work environment might result in more serious health problems.

IV. HEALTH HAZARD EVALUATION

A. Process Description

In the Screen Print Preparation Department, 100 percent polyester fabric is disperse dyed a solid color and then dried in preparation for additional finishing in the Soaping Department. The white polyester fabric that enters the Screen Print Preparation Department has previously been bleached, scoured and treated with a chemical flame retardant. After these pretreatments, no residues or contaminants should remain on the fabric; however, some sizing materials, oils or additives from previous operations may remain.

The feed-in operator runs a single roll of polyester fabric into the "scray" at an accelerated rate by means of a variable speed electric motor drive assembly. The scray is a storage device which allows for the in-process accumulation of fabric and thus, provides for the continuous operation of the disperse dyeing process while the feed-in

operator is adding a new roll of fabric. The new fabric roll is simply sewn to the previous roll by the feed-in operator with a pneumatic sewing machine. Before the fabric is dyed, it passes under a series of ultraviolet lamps (special fluorescent tubes) to detect oil or grease residues from previous operations. The fabric is then directed into the dyebath and through a dye pad (pressure rollers) which distributes the dyestuff uniformly throughout the fabric.

The dyestuff contains one or more dyes, a dye carrier, and anti-migration and anti-foaming agents. It is formulated atop an elevated mixing platform by the dye mix operator. The various dye batch ingredients are scooped out of their containers, using plastic cups, and weighed on a balance prior to being poured into a large, plastic mixing bucket. However, one component, Levalin VKL[®], is transferred to the mixing bucket via an electric pump. After the chemicals have been thoroughly mixed and diluted with water, the bucket is emptied by hand into a large dye vat which is used to fill the paddler dyebath.

The fabric is then passed through a Fostoria[®] pre-dryer which uses quartz tubes to generate infrared radiation to partially dry the fabric by radiant heat. Local exhaust ventilation has been installed immediately after the Fostoria[®] pre-dryer to remove water vapor and other volatile components of the dyebath. The fabric is then passed through the Famatex[®] hot house tenter frame at an approximate temperature of 204°C (400°F) for about 30 seconds. The tenter frame is approximately 27.5 meters (90 feet) long and is composed of two continuous parallel chains with clips which grasp the fabric and hold it at a desired width to prevent shrinkage while the fabric is dried and heat set. The fabric is finally directed to a folding machine which is monitored by the take-off operator.

It should be noted that the dyestuff used during the period of this evaluation did not contain a flame retardant. Previously, a flame retardant such as Antiblaze 19 or 191[®], or Pyrovatex 388[®], was added to all polyester dyestuffs and on a weight-weight basis was the primary constituent of the dye mixture. However, the company now purchases a polyester fabric which has been pre-treated with a flame retardant.

B. Evaluation Design

In response to this request, an initial visit to the plant was conducted on May 18, 1977 by the Industrial Hygienist from the NIOSH regional office in Atlanta, Georgia. A walk-through survey was performed in the Screen Print Preparation Department and all first and second shift production employees were privately interviewed and health forms completed. The results of this initial screening survey, as reported in an Interim Report of December 1977, indicated that a follow-up survey would be required.

Because of a manpower shortage in the NIOSH Region IV Office, follow-up investigators were assigned from the NIOSH Hazard Evaluation and Technical Assistance Branch in Cincinnati, Ohio. The new investigators assigned to this project were Mr. Richard Taft, Industrial Hygienist and Elva Elesh, M.D.

On January 25 - 27, 1978 a follow-up environmental and medical survey was conducted in the Screen Print Preparation Department. An opening conference was conducted and was attended by representatives of both management and labor. Following the opening conference, a walk-through survey was performed by the newly assigned NIOSH investigators.

C. Evaluation Methods

1. Environmental

Environmental sampling was conducted in the Screen Print Preparation Department on January 26, 1978. Employee exposure to solvent vapors and thermal decomposition products from the dye bath were measured via personal, area, and bulk air samples which were collected during the 7:00 am - 3:00 pm shift in the vicinity of the #2 Famatex[®] machine. Multiple collection media were utilized due to the unknown nature of the prospective chemical contaminants.

Employee exposure to organic solvent vapors and thermal decomposition products of the dyestuff, was evaluated by adsorbing the vapors onto activated charcoal or Florisil[®] media contained in glass sampling tubes. Vacuum sampling pumps were utilized to draw air through the sampling tubes at a flow rate of 50 milliliters per minute for personal and area samples, and at 1.0 liter per minute (LPM) for bulk air samples. Personal air samples were collected in the breathing zone of the exposed employees, while area and bulk air samples were collected in locations adjacent to the #2 Famatex[®] machine in an effort to characterize the general work environment. These air samples were transmitted to the NIOSH laboratory in Cincinnati and subsequently analyzed by gas chromatography and mass spectrometry.

Employee exposure to airborne concentrations of diazonium salts and azo dye particulates was evaluated by drawing air through duplicate AA (37 millimeter diameter, 0.8 micron average pore size - mixed cellulose ester) filters. Vacuum sampling pumps were utilized to draw air through the filters at a flow rate of 1.5 LPM for both personal and area air samples. Personal air samples were taken in the breathing zone of the exposed employees, while area air samples were taken adjacent to the #2 Famatex[®] machine. A bulk sample of the dyestuff used during the period of this evaluation was also obtained and was used to establish a standard calibration curve. These duplicate filter samples were transmitted to the NIOSH laboratory in Cincinnati and were analyzed by a NIOSH spectrophotometric method.¹

*Mention of a commercial product does not constitute endorsement by the National Institute for Occupational Safety and Health.

For screening purposes, direct reading Dräger[®] detector tubes were utilized to evaluate atmospheric levels of the following substances: formaldehyde, isopropanol, sulfur dioxide, phosphine, benzene and phenol.

2. Medical

After medical review of the twelve employee interview forms obtained during the initial survey of May 18, 1977, it was determined that employee complaints were consistent with exposure to an irritant substance. Therefore, a medical examination of the affected employees during and after the dyeing process was indicated.

Accordingly, on January 26, 1978, the NIOSH physician was present in the plant prior to start-up of the dyeing process. Of the twelve workers who completed the employee interview form during the initial survey, nine were seen again. Five were interviewed on the 7:00 am - 3:00 pm shift and four on the 3:00 pm - 11:00 pm shift. Three of the employees were not interviewed, as two were on the 11:00 pm - 7:00 am shift and one was absent.

D. Evaluation Criteria

The concept that there are concentrations of air contaminants to which most employees may be exposed on a day-to-day basis, without discomfort or adverse health effects, is fundamental to the practice of industrial hygiene. Airborne exposure limits for many chemical substances encountered occupationally have been recommended or promulgated by several organizations. These limits are normally expressed as a time-weighted average (TWA) exposure for a normal 8 to 10 hour workday, or 40 hour workweek, and are presumed to be valid throughout a normal working lifetime. However, it should be noted, that due to a wide variation in individual susceptibility, a small percentage of employees may experience discomfort from exposure to some substances at concentrations at or below the recommended or promulgated standard; a smaller percentage may be affected more seriously by aggravation of a pre-existing condition or by development of an occupational illness.

For this investigation, environmental evaluation criteria were considered from the following sources: (1) NIOSH Criteria Documents with recommended occupational exposure standards, (2) American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Values (TLVs) with their supporting documentation, and (3) U.S. Department of Labor - Occupational Safety and Health Administration (OSHA) Standards. For the chemical substances evaluated during this investigation, the primary environmental criteria selected were:

<u>Chemical Substance</u>	<u>Environmental PPM**</u>	<u>Standard mg/M³***</u>	<u>Reference Source****</u>
Benzene	1.0	3.2	(1)
Xylene	100.0	435.0	(1,2,3)
Decane	NS*	NS	--
Undecane	NS	NS	--

*No standard has been recommended.

**Parts of vapor per million parts of contaminated air by volume at 25°C and 760 mmHg.

***Approximate milligrams of substance per cubic meter of air.

****Reference numbers in parentheses refer to the source(s) from the above discussion from which the environmental standard was obtained.

Environmental air sampling during the dyeing process has identified the presence of the following chemicals in the work area: benzene, xylene, decane and undecane. The following discussion is provided so that the employees of the Screen Print Preparation Department may better understand the potential health hazards associated with excessive occupational exposure to these chemical substances.

BENZENE -- is a flammable, colorless, highly toxic aromatic liquid. Benzene can enter the body by all three routes of absorption: inhalation, ingestion, and by direct skin contact. In industry, the major route of entry is by inhalation of the vapor; however, skin absorption may also be of significance. Excessive exposure to benzene may result in central nervous system depression and skin irritation. Recent evidence has shown that benzene is leukemogenic. Because of the possibility of causing leukemia, a progressive malignant disease of the blood-forming organs, NIOSH recommends that for regulatory purposes, benzene be considered carcinogenic in man. NIOSH also recommends that exposure to benzene be kept as low as possible, and that no worker be exposed to a concentration greater than 1 ppm in air. One ppm represents the lowest level at which a reliable estimate of occupational exposure to benzene can be determined at the present time. This concentration is a ceiling value and as such, should never be exceeded.^{2,3} The ACGIH (1977) recommended TLV is 10 ppm and is expressed as an 8 hour TWA exposure. It should be noted, however, that the ACGIH has classified benzene as a suspected human carcinogen and suggests that employee exposure be carefully controlled to levels consistent with the animal and human experience data.^{4,5} The present Federal Standard, as promulgated by OSHA, is 10 ppm as an 8 hour TWA with an acceptable ceiling concentration of 25 ppm. A maximum peak concentration of 50 ppm is permitted, provided that the duration is 10 minutes or less, for an 8 hour work shift.⁶ In May of 1977, OSHA promulgated an Emergency Temporary Standard for benzene and adopted the NIOSH recommended ceiling concentration of 1 ppm.⁷ However, OSHA's emergency standard has been stayed by the U. S. Court of Appeals for the Fifth Circuit on April 18, 1978, until the court rules on the standards validity.⁸

XYLENE -- is a flammable, colorless, aromatic liquid of slight to moderate toxicity. It has many physical and chemical properties similar to those of benzene; however, it does not produce the blood disorders characteristic of benzene absorption. The primary routes of absorption are from inhalation of the vapor and direct skin contact. Exposure to high concentrations of xylene vapor may result in irritation to the eyes, nose and throat, and depression of the central nervous system. NIOSH recommends adherence to the present OSHA standard of 100 ppm as a TWA exposure for up to a 10 hour workday, and 40 hour workweek. Additionally, NIOSH recommends a ceiling concentration of 200 ppm as determined during a 10 minute period.^{6,9} The environmental criteria recommended by the ACGIH (1977) is a TLV of 100 ppm as determined by an 8 hour TWA exposure, and a Short Term Exposure Limit (STEL) of 150 ppm. The STEL is a maximum allowable concentration, or ceiling value; which may not be exceeded during a 15 minute excursion period.^{4,5}

DECANE -- is a flammable, colorless, liquid of relatively low toxicity. Decane has been classified as a simple asphyxiant, and exposure to high vapor concentrations may result in depression of the central nervous system.¹⁰ Environmental criteria have not been promulgated or recommended for occupational exposure to this chemical substance. Generally, an occupational exposure limit is not required for simple asphyxiant gases because they act by simply excluding oxygen from the lungs. The oxygen content of inspired air may be reduced to two-thirds of its normal value before appreciable adverse health effects occur and this requires that the simple asphyxiant be present at a concentration of 33 percent in the mixture of air and gas.¹⁰ The ACGIH (1977) recommends that the minimal oxygen content should be 18 percent by volume under normal atmospheric pressure.⁴

UNDECANE -- is a combustible, colorless, aliphatic hydrocarbon liquid of relatively low toxicity and has many physical and chemical properties similar to those of decane.¹⁰ Aliphatic hydrocarbons are in general, simple asphyxiants, skin irritants and central nervous system depressants. Prolonged skin contact may also result in dermatitis, due to defatting of the skin.¹¹ Environmental criteria have not been promulgated or recommended for occupational exposure to this substance.

When two or more hazardous substances are present, their combined effect, rather than that of either substance individually, should be given careful consideration. In the absence of information to the contrary, the effects of the different hazards should be considered as additive. The sum of the fractions of measured atmospheric concentration of contaminant over the corresponding threshold limit value ($C_1/T_1 + C_2/T_2 + \dots + C_n/T_n$) should not exceed unity. Exceptions to this rule may

be made when there is a good reason to believe that the toxicological properties of the chemical substances are not in fact additive, but independent.⁴ Therefore, carcinogenic substances such as benzene and simple asphyxiants like decane and undecane, are excluded from this relationship.

E. Evaluation Results and Discussion

1. Environmental

Qualitative analysis of four charcoal tube bulk air samples (CT - 1, 4, 12, 13) by gas chromatography and mass spectrometry (GC/MS) has indicated four major and numerous minor peaks. The four major peaks have been identified as: benzene, xylene, decane and undecane. Numerous minor peaks, which correspond to other aromatic and aliphatic compounds, have also been identified. Trace amounts of toluene and naphthalene were also detected. It should be noted that in GC/MS analysis, peak area is directly proportional to concentration. Therefore, the four major peaks correspond to the highest environmental concentrations.

Quantitative analysis of personal and area charcoal tube samples by gas chromatography, for the chemical substances previously identified, indicate airborne concentrations of less than 1.0 percent of the environmental criteria and are thus, not considered to constitute a health hazard during the period of this evaluation. Results from the personal breathing zone and area charcoal tube samples are shown in Table I.

Qualitative analysis of the Florisil[®] bulk air samples by GC/MS indicated the presence of a very high boiling point compound. The mass spectrum indicates that it is a high molecular weight compound (above 300) and is chiefly aliphatic. No phenyl groups or ring structures were detected, however certain mass spectral fragments indicated the possibility of iodide and a hydroxyl group within the molecule. The NIOSH laboratory has been unable to identify this unknown substance and suggests that it is probably a reaction product from the dyestuff. The maximum environmental concentration has been estimated at 0.05 ppm and therefore, due to its aliphatic properties, should not constitute a health hazard during the period of this evaluation.

The analysis for azo dyes and diazonium salts utilizes a NIOSH spectrophotometric method. Diazonium salts exhibit maximum absorption at a wavelength of 375 nanometers (nm), while azo dyes exhibit maxima in the 400 - 700 nm range, the exact wavelength being dependent on the chemical structure of the dye molecule. Quantitative analysis of the duplicate filter samples revealed that no absorption maxima were observed at these wavelengths. Therefore, the results of personal and area air samples, as shown in Table II, indicate that there was no measurable exposure to azo dyes or diazonium salts during the period of this evaluation.

Direct reading detector tubes were utilized to evaluate the following substances: formaldehyde, isopropanol, sulfur dioxide, phosphine, benzene and phenol. A positive indication was obtained only from the phenol detector tube. However, this response was later determined to be due to an interfering agent and not to phenol. Subsequent laboratory analysis indicated that no phenolic compounds were present in the dyestuff (Tan 61542M).

2. Medical

None of the workers seen by the NIOSH physician had any complaints on this particular day, and several stated that they had had none for some considerable time. A number specifically said that their symptoms were associated with, or aggravated by, the inclusion of the flame retardant, Antiblaze 19 or 19[®] or Pyrovatex 388[®], in the dye mixture. The use of these flame retardants was discontinued during the summer of 1977.

The NIOSH physician visited the First Aid Room, which is staffed by three full-time nurses - one on each shift. It was determined from two of the nurses that the symptoms of which the workers complained had not been severe enough for them to seek medical attention, which fact was confirmed by the workers. Nor had any worker been affected to the extent of leaving the work environment at any time.

The NIOSH physician and industrial hygienists did not experience eye or upper respiratory tract irritation during the dyeing operation. It should be noted, however, that a particularly pale dyestuff was used on this date (Tan 61542M).

Nevertheless, it must be considered that the workers had been exposed to some irritant substance(s) and/or agent(s) in the past. It is the opinion of the NIOSH physician that the effects of such exposure are transient in nature and thus, no long-term adverse health effects would be anticipated.

F. Conclusion and Recommendations

Thorough analysis of the data obtained from environmental sampling and worker interviews indicated that a health hazard to the employees in the Screen Print Preparation Department of the Rock Hill Printing and Finishing Company, did not exist during the period of this evaluation. The following recommendations are made to help improve the health and safety conditions in the employees work environment:

1. Occupational exposure to benzene should be kept as low as possible and whenever identified in the work environment, as in the charcoal tube bulk air samples, it should be replaced with less toxic substitutes whenever feasible. The benzene identified in the bulk air samples is probably the result of a polymer decomposition reaction; however, the management should review all chemical products used to formulate the dyestuff to insure that benzene is not present as an actual ingredient.

2. An educational program should be developed to inform the employees of the hazards associated with the chemical substances encountered in the work environment and good employee work practices should also be discussed and encouraged.

3. The mixing operator was not wearing any personal protective equipment while formulating the dye mixture. During this mixing process, eye contamination could easily occur. One of the ingredients of this mixture, Levalin VKU[®], was stored in a large drum which was clearly labeled "Skin and Eye Irritant". The Material Safety Data Sheet, under the heading of Health Hazard Data, gives the following information on Levalin VKU[®]. "Skin irritation" slight to moderate reaction. Eye irritation: severe reaction. In case of contact with skin, wash well using a suitable cleansing agent. In case of contact with the eyes, flush with water and get prompt medical attention". Therefore, employees engaged in dyestuff formulation should be provided with and required to wear a chemical face shield or goggles and impervious gloves.

4. A functional emergency eye bath was present on the mixing platform. However, it was partially occluded, as many soiled rags had been heaped upon it. This device should be kept clear of all obstructions.

5. The fire extinguisher was observed on the floor of the mixing platform and did not have a service inspection tag. This device should be permanently mounted in a conspicuous place and should be inspected and recertified.

6. As the mixing platform is an elevated structure, a steel toe board and guard rail should be installed on the open, loading end of the platform. This should help to minimize accidents for employees working on and below the mixing platform.

7. The fluorescent light fixture which is positioned over and in near proximity to the two large mixing tanks, should be equipped with a plastic shield to protect the employees in the event the fluorescent tubes are broken.

8. While not required by OSHA regulations, Material Safety Data Sheets should be obtained from all chemical suppliers. This information can be beneficial in assessing the toxicity or hazards encountered in working with a particular chemical product.

9. The suspended electrical cord which supplies power to the electric motor on the scray, should be securely fastened and routed in accordance with good electrical work practices.

The NIOSH staff would like to thank both management and labor for their cooperation and assistance during this evaluation.

V. REFERENCES

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TABLE I

Results of Personal and Area Air Sampling for Exposure to Organic Vapors

Rock Hill Printing and Finishing Company
Screen Print Preparation Department
Rock Hill, South Carolina

January 26, 1978

TIME WEIGHTED AVERAGE EXPOSURE IN PPM¹

Sample Number	Description/Location	Time	Volume (Liters)	Benzene	Xylene	Decane	Undecane
C2	Area - #2 Famatex Take-off End	0822-1426	20.08	ND ²	0.23	ND	ND
C3	Area - Between new Hot Frame #12 and Famatex #2	0818-1428	23.34	ND	ND	ND	ND
C5	Area - Tenter Frame Input	0816-1430	22.33	ND	0.10	ND	ND
C6	Area - Vicinity of Scray Operator	0814-1432	20.72	ND	ND	ND	ND
C7	Personal - Scray Operator	0814-1422	18.69	ND ³	ND ³	ND ³	ND ³
C8	Personal - Take-off Operator	0828-1428	7.67	ND ³	ND ³	ND ³	ND ³
C9	Area - Desk near exit	0852-1428	19.23	ND	0.12	ND	ND
C10	Personal - Dye Mixer	1037-1105	28.00	ND	0.08	ND	ND
C11	Personal - Dye Mixer	1037-1105	28.00	ND	0.08	ND	ND
C14	Blank Charcoal Tube	--	--	ND	ND	ND	ND

1. PPM - Parts of vapor per million parts of contaminated air by volume at 25°C and 760 mm Hg.
2. ND - none detected, less than the lower limit of detection of 0.01 milligram per sample.
3. Vacuum pump malfunctioned.

TABLE II

Results of Personal and Area Air Sampling for Exposure to Diazonium Salts and Azo Dyes

Rock Hill Printing and Finishing Company

Screen Print Preparation Department

Rock Hill, South Carolina

January 26, 1978

TIME WEIGHTED AVERAGE EXPOSURE IN MG/M³¹

Sample Number	Description/Location	Time	Volume (Liters)	Azo Dyes	Diazonium Salts
A1	Area - #2 Famatex Take-off End	0822 - 1426	546	ND ²	
A2	Area - " " " "	0822 - 1426	546		ND
A3	Area - Between new hot Frame #12 and Famatex #2	0818 - 1428	555	ND	
A4	Area - " " " " " "	0818 - 1428	555		ND
A5	Area - Tenter Frame Input	0816 - 1430	561	ND	
A6	Area - " " " "	0816 - 1430	561		ND
A7	Area - Vicinity of Scray Operator	0814 - 1432	567	ND	
A8	Area - " " " "	0814 - 1432	567		ND
A9	Personal - Scray Operator	0814 - 1422	491	ND	
A10	" " " "	0814 - 1422	491		ND
A11	Personal - Take-off Operator	0828 - 1425	426	ND	
A12	" " " "	0828 - 1425	426		ND
A13	Area - Desk Near Exit	0848 - 1428	510	ND	
A14	" " " "	0848 - 1428	510		ND
A15	Blank Filter	--	--	ND	
A16	" " " "	--	--		ND

1. MG/M³ - approximate milligrams of substance per cubic meter of air.

2. ND - none detected, lower limit of detection for azo dyes and diazonium salts is 0.69 and 0.75 milligrams per sample (dry weight), respectively.