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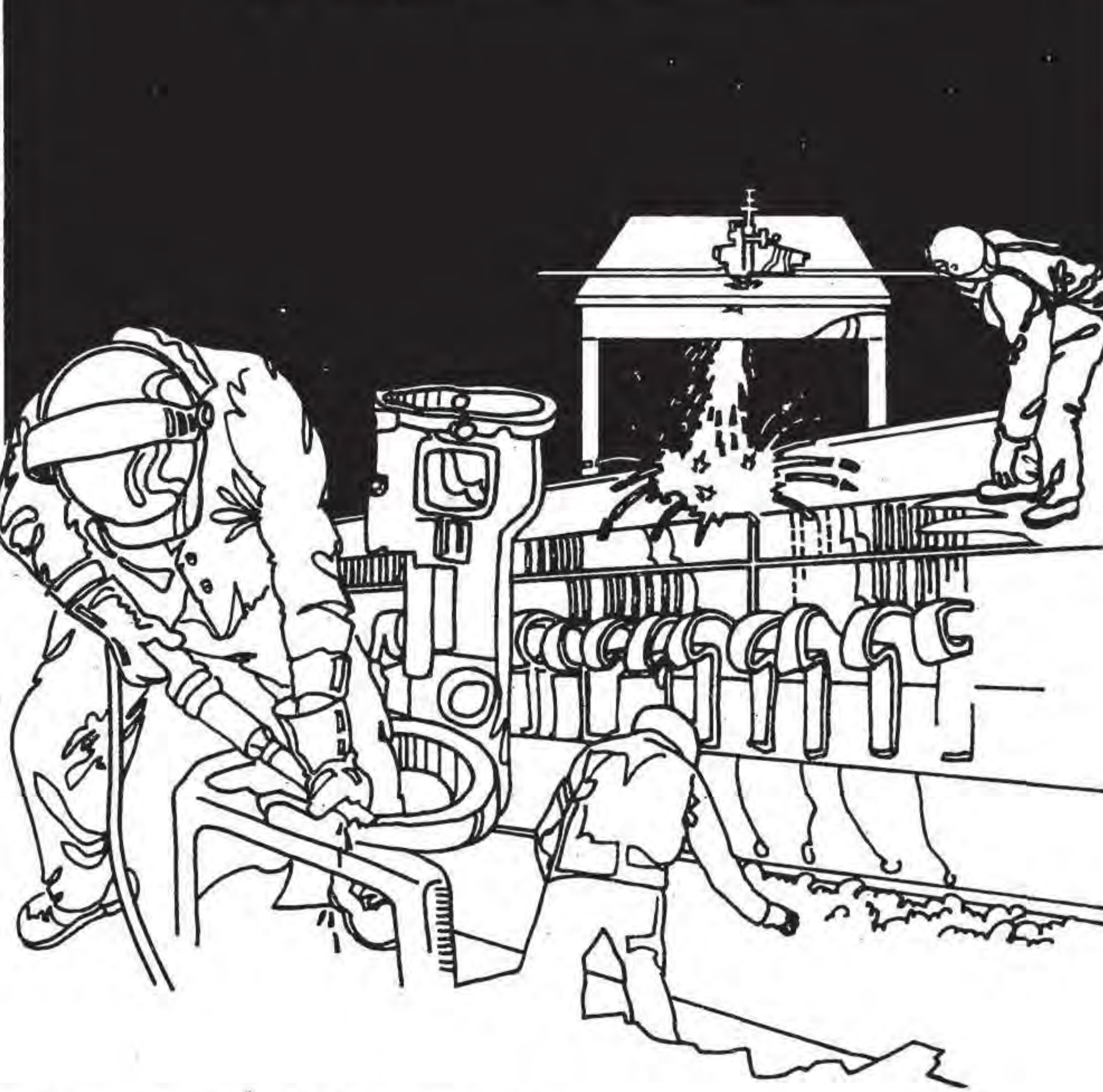

Health Hazard Evaluation Report

HETA 81-399-1172
RIDGWAY COLOR COMPANY
RIDGWAY, PENNSYLVANIA

PREFACE

The Hazard Evaluations and Technical Assistance Branch of NIOSH conducts field investigations of possible health hazards in the workplace. These investigations are conducted under the authority of Section 20(a)(6) of the Occupational Safety and Health Act of 1970, 29 U.S.C. 669(a)(6) which authorizes the Secretary of Health and Human Services, following a written request from 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 Hazard Evaluations and Technical Assistance Branch also provides, upon request, medical, nursing, and industrial hygiene technical and consultative assistance (TA) to Federal, state, and local agencies; labor; industry and other groups or individuals to control occupational health hazards and to prevent related trauma and disease.

Mention of company names or products does not constitute endorsement by the National Institute for Occupational Safety and Health.

HETA 81-399-1172
AUGUST 1982
RIDGWAY COLOR COMPANY
RIDGWAY, PENNSYLVANIA

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I. SUMMARY

On July 27, 1981, the National Institute for Occupational Safety and Health (NIOSH) received a request for a Health Hazard Evaluation from the United Steel Workers of America (USWA) Local 13694. There was concern that workers at the Ridgway Color Company in Ridgway, Pennsylvania were experiencing an unusually high rate of death from cancer. This concern was compounded by the identification of 3,3'-dichlorobenzidine (DCB) as a suspect carcinogen by the Occupational Safety and Health Administration (OSHA), since DCB had previously been handled in the plant as a benign chemical intermediate.

The medical evaluation consisted of an interviewer-directed questionnaire administered to a non-random sample of workers, and a cancer mortality study. Urine samples were also collected to detect any presence of DCB.

The environmental evaluation consisted of (1) area and personal air sampling for DCB, hydrochloric acid (HCL) and total dust, (2) analysis for trace contamination with potential carcinogens in bulk samples of pigment intermediate, (3) analysis of diarylide yellow presscake for DCB, and (4) a characterization of ventilation and work practices.

Medical findings were consistent with symptoms of upper airway and eye irritation: 59% of the interviewed workers reported more than five episodes of eye irritation in the prior twelve months; 55% had more than five episodes of nasal irritation during the same time period. An unusual rate of death from cancer, particularly from cancer of the bladder, was not detected. No DCB was detected in any of the urine samples at the limit of detection (10 ng/ml). DCB was not detected in workplace air at the limit of detection (10 ppm). The environmental evaluation did not indicate high levels of HCL or irritant dust. Hydrochloric acid was not identified at an estimated detection limit of 4 micrograms per sample; the highest recorded level of total dust was 0.004 mg/M3 (8 hour TWA). The level of contamination of chemical intermediates with known or suspect carcinogens was low. Neither alpha nor beta-naphthylamine were detected. Para-toluidine was detected, but in amounts not exceeding 40 ug/g of intermediate.

An evaluation of cancer mortality at pigment plant utilizing dichlorobenzidine , an intermediate, did not detect an unusual rate of cancer and detected no cases of bladder cancers. Contamination of intermediates with known or suspect carcinogens was low.

KEYWORDS: SIC 2865 (Amines, benzidine bladder cancer, 3,3'-dichlorobenzidine, mucosal, muriatic acid, respiratory, toluidines.)

II. INTRODUCTION

On July 27, 1981, NIOSH received a request for a Health Hazard Evaluation from an authorized representative of the employees at the Ridgway Color Company of Ridgway, Pennsylvania. Workers at the Ridgway facilitated are representated by Local 13694 of the United Steel Workers of America. There was a concern over increased cancer risks to current and retired employees engaged in the production of pigments for the printing industry. There were particular questions about the association between 3,3'-dichlorobenzidine (DCB) and the development of bladder cancer. Prior to 1978, the chemical was handled without control precautions. It was subsequently recognized as a suspect carcinogen and processed under isolation conditions with storeroom handling and charging being performed by a single worker with supplied air respiration. A corollary issue was whether the large proportion of the workforce facing retirement in the next 5-10 years would require special surveillance, given their earlier exposures to DCB. There was also concern about toxic chemicals, particularly acids, used in production.

Environmental and medical investigations were conducted by NIOSH representatives on September 15-16, 1981 and on December 16-17, 1981.

III. BACKGROUND

The Ridgway Color Company began operations in 1947 as a manufacturer of plastics and organic pigments. Current production involves only organic non-metallic colors, both in flushed and dried form, for use in the printing industry. In addition, a small varnish operation -- Pope and Gray Varnish -- provides varnish for internal use and limited sale. A plastic and rubber colorant facility was transferred to Maryland in 1969, after Ridgway was purchased by Wheelabrator-Frye -- its present owner.

Ridgway employs approximately one-hundred production workers and thirty to forty salaried workers. Work is divided over three shifts: sixty percent of the work force is assigned to the day shift, twenty percent to the evening and night shifts. The general stability of the Ridgway working population is recognized in worker seniority -- 25% having worked longer than 20 years and more than 50% having worked more than 10 years.

Ridgway produces three principal types of colors: phthalocyanine blues and greens; two diarylide yellows -- Pigment Yellow 12 and 14 -- which use DCB; and several azo red pigments. Bromofluorescein and phloxine pigments were produced in the 1970's but have since been discontinued.

DCB, the base for the diarylide yellows, is charged, diazotized and coupled with acetoacetanilide in a sealed environment. The single tank operator is equipped with a supplied air respirator. The process was approved as adequate for DCB handling by the Occupational Safety and Health Administration (OSHA) in November, 1978. A new azo making facility, which will eventually house diarylide production was placed into partial on-line use between the initial and follow-up visit of the NIOSH investigators, but no DCB has as yet been handled in the new facility.

All azo pigment production involves the use of finished intermediates: there is no actual chemical synthesis taking place at Ridgway. Increasingly these intermediate chemicals, which include -- beta naphthol, beta napththoic acid, Tobias acid, acetoacetanilide and several sulfonated amino-toluene bases -- are of foreign manufacture, and Ridgway does not maintain material safety data sheets on them. This is of more than passing importance, since several known carcinogens are near isomers to these bases and could be unrecognized contaminants without a high level of quality control.

Ridgway Color maintains a limited medical surveillance and medical records program. Health status is evaluated in pre-employment physicals and in yearly physical exams: there is no discharge exam. In 1978, Ridgway introduced an OSHA approved DCB screening protocol. It consists of the analysis of semi-annual collected urine for both occult blood and abnormal bladder cells (urine "PAP" smears). Screening includes tank operators, labor pool workers who directly handle DCB, and lab workers. The company maintains no long-term file on deaths and disability.

IV. EVALUATION DESIGN AND METHODS

A. Environmental

Sampling methods employed in the environmental survey are described below:

1. 3,3'-dichlorobenzidine - "DCB" was sampled using a combo to a glass fiber filter and silica gel tube for particulate and vapor respectively. Personal sampling pumps were used at a flow rate of 200 cc/minute for the duration of each work operation.

The samples were analyzed for 3,3'-dichlorobenzidine by a modification of NIOSH Method P&CAM 246.

The standards were prepared by placing aliquots of solution of 3,3'-dichlorobenzidine on glass fiber filters and in silica gel tubes. The standards were then desorbed and analyzed with the samples.

The sample and standard silica gel tube contents were desorbed in 2 mL of methanol and analyzed in this form, while the glass fiber filters were desorbed in 2 mL of methanol and filtered through a 5 micron nylon filter; all samples and standards were then injected into a high pressure liquid chromatograph under the following conditions:

Solvent Delivery:	Perkin-Elmer Series 3-B Pump Module
Mobile Phase:	methanol/water
Flow Rate:	1 mL/min.
Column:	Supelco C_{18}, 250 x 4.6 mm, 5 micron particles
UV Detector:	Perkin-Elmer LC-75
Detector Wavelength	280 nm @ 0.04 AUFS

The limit of detection for this analysis of 3,3'-dichlorobenzidine was 1 microgram/sample.

2. Hydrogen Chloride - "HCL": - was sample using silica gel tubes and personal sampling pumps at a flow rate of 200 cc/min.

Samples collected on silica gel tubes were analyzed for hydrogen chloride by ion chromatography. NIOSH Method P&CAM No. 310 was followed in preparing the samples, blanks and standards. A series of chloride standards covering the range 0.4 to 20 micrograms Cl-/mL were prepared.

Ion chromatograph working conditions were as follows:

Eluent:	0.003 M $naHCO_3$/0.0024 m na_2CO_3 @ 30% flow rate.
Columns:	4 X 50 mm fast-run anion precolumn 4 X 100 mm anion suppressor
Chart Speed:	30 cm/hr.
Detector Setting:	3 mho/cm (FS)
Retention Time:	3.8 minutes
Injection Volume:	100 microliters

A detection limit of 4 micrograms HCL per sample is estimated.

3. Total Dust (pigment) Gravimetric - was sampled at 1.5 liters per minute using personal air sampling pumps and a 0.8u filter, cassette assembly.

The total weights of the samples were determined by weighing the samples plus the filters on a Perkin-Elmer Model AD-2 electro-balance and subtracting the previously determined tare weights of the filters. The tare and gross weighings were done in duplicate.

The instrumental precision of weighings done at one sitting is 0.01 mg. Due to variable factors such as overloading, hygro-scopyicity of sample, humidity, and the physical integrity of the filter itself, the actual precision can be considerably poorer and occasional slight net negative particulate weights are to be expected.

The bulk samples of "Bona", B-Naphthol, and Tobias Acid were sonicated 30 minutes in 2 mL carbon disulfide. The clear supernatent liquid was analyzed by gas chromatography according to a modified NIOSH Method 264 using standards of alpha and beta napthylamine dissolved in carbon disulfide.

The analysis was performed using a Hewlett-packard gas chromatograph equipped with a flame ionization detector. A 10' X 1/4" glass column packed with 3% AN600 on 100/120 Chromosorb W HP was used with the oven manually programmed from 190^{0}C to 260^{0}C at a rate of 32^{0}C per minute.

4. The ethanol extracts of weighed portions of the sample bulks of "C" Amine, 4-B Acid and 2-B Acid were analyzed by gas chromatagraphy using NIOSH Methods 168 with the following modifications:

Extraction Process:	A weighed quantity of each sample was added to 95% ethanol (200 mg to 400 mg of sample per mL of ethanol). The mixtures were sonicated for 30 minutes and then centrifuged. The supernate was used for direct injection without further treatment. The efficiency of this esxtraction procedure is unknown. Liquid standards were used to quantitiate the sample results.
Gas Chromatograph:	Hewlett-Packard Model 5731 equipped with a flame ionization detector and accessories for capillary column use.
Oven Conditions:	150^0 isothermal
Other:	Helium was used as the carrier gas in the split mode of operation with a split ratio of 10:1.

The bulk sample of Diarylide yellow presscake was analyzed for 3,3'-dichlorobenzidine by modifications of NIOSH Method P&CAM 246. The sample was received in bulk form.

Standards were prepared by diluting aliquots of a solution of 3,3'-dichlorobenzidine with 2 mL methanol. The standards were analyzed with the samples.

The sample was prepared by dissolving a known amount of the bulk sample in 10 mL of methanol. The sample was then filtered through a 0.5 micron nylon filter. Aliquots of the sample and standards were injected into a high pressure liquid chromatography system under the following conditions:

Solvent Delivery:	Perkin-Elmer Series 3-B Pump Module
Mobile Phase:	methanol/water
Elution:	isocratic
Flow Rate:	1 mL/min
	Supelco C_{18}, 250 X 4.6 mm, 5 micron
UV:	Perkin-Elmer LC-75
Detector Wavelength:	280 nm @ 9194 AUFS

The limit of detection for this analysis of 3.3'-dichlorobenzidine was 0.1 milligram/gram.

5. All ventilation measurements were taken with a Alnor Senior velometer.

The environmental area sampling strategy for bulk samples taken on December 17, 1981 is presented below:

1."DCB" (3,3, Dichlorobenzidine) operations - drum emptying and drum transfer operators - for exposures to DCB.

2.Tank floor operations - "Ruben Red" operator, "Barium lithol" (new and old units) operators and "Salt Grinding" operator - for exposures to HCL (hydrogen chloride gas).

3.Barium Lithol - Dryer operator ("dumping out") and Blender and crusher operator - for total dust (pigment) (gravimetric).

4.Bulk Samples of "Bona", Beta-Naphthol and Tobias Acid for analysis for alpha and beta naphthylamine.

5.Bulks sample of "C" Amine, 4_7B Acid and 2B-Acid for analysis for o-and p-Toluidine.

6.A bulk of sample Diarylide "Yellow" presscake for analysis of DCB (dichlorobenzidine) content.

Ventilation measurements were taken at both reaction and transfer vessel sites. Local exhaust measurements in the "dumping out" and salt grinding areas were also taken.

B. Medical

An interviewer-directed medical screening questionnaire was administered to twenty-two Ridgway production workers on September 15-16, 1981. Workers were selected by the NIOSH investigator from the current seniority list without randomization in an effort to obtain a representative sample from all work areas and age groups. Questions were directed towards present and previous occupational experience, medical history and habits, current general medical symptoms and the presence of urinary tract symptoms. Workers were also questionned about the use of respirators and about plant and personal hygiene.

A limited epidemiological survey was undertaken in order to consider the cancer risks to Ridgway workers. Cases were determined by recording all names from a union obituary list; the diagnosis was confirmed by first contacting surviving immediate family members, then contacting the attending local physician for confirmation. Total person years at risk could not be calculated from a single source because the company had not maintained an employee file dating back to the opening of the plant, whereas the tenure of several of the deceased because worker employment exceeded the duration of company record keeping. Person years were estimated by first assembling a list of names from the current seniority list for production workers and salaried personnel with plant experience. All workers whose names appeared in the union membership log from 1947, but who were not currently employed, were added to the list. Anyone who had moved out of the area and might conceivably be lost to the Union's log of deceased members was contacted by telephone and survival was verified. Because Union records did not include transient, short-term employees, and a review of Ridgway's recent personnel history showed that turn-overs generally came from workers with under two years experience, a two year work history was a requirement for entry into the cohort. The same exclusion requirement was applied to cases. The entire group was randomized and a sample of 30 names was selected. The group was small enough for the accurate determination of the age and employment history of both the currently employed and those who had retired or were dead or disabled. This information was then extrapolated to the entire Ridgway work force, both past and current.

An additional measure of potential worker exposure involved the collection of urines for determination of DCB concentration. Twenty specimen containers were administered to day-shift workers at the conclusion of the work-day and collected, following a double voiding protocol, at the beginning of work on the following morning. Two samples were also collected as standardized controls from non-production workers. Selection was not random, but involved workers from a representative selection of work-sites.

V. EVALUATION CRITERIA

A. Medical

A brief review of known toxic effects of substances to which Ridgway workers are potentially exposed follows.

1. 3,3'-dichlorobenzidine: Because of its structural similarity to benzidine, a known human bladder carcinogen, DCB is considered as a suspect carcinogen. Animal and in vitro biological assays substantiate both a mutagenic and carcinogenic potential for DCB (2,3,4,). However its effects seem less mareked than benzidine and two studies of DCB exposed worker populations, involving more than 400 people, have not uncovered a case of bladder cancer (5,6).

2. Diarylide Yellow Pigments: The breakage of azo bonds by human gut bacteria and liver, with subsequent recovery of the liberated base in urine is a phenomenon that has been observed with benzidine, dianisidine and o-tolidine dyes. A similar effect has been observed with Direct Red 46, a dye based on DCB. However, in both long and short-term animal feeding studies with diarylide yellow pigment, there has been neither an observed excess rate of cancer nor recovery of free DCB in urine (7,8,9,10). An important qualification to these results is the the report by Akiyama that Japanese diarylide yellow workers did have recoverable aromatic amines in their urine (11). However, the exact identity of these amines was not determined.

3. Tobias Acid (2-Naphthylamine - 1- sulfonic acid): Developed as a substitute for Beta-naphthylamine (BNA), Tobias acid is used as a pigment intermediate in the production of Pigment Red 49 at Ridgway. Despite its structural similarity to BNA and high rate of intestinal absorption, Tobias Acid has been recovered in animal urine without evidence for metabolic activation (12). Further evidence for an absence of carcinogenic hazard is seen in negative biological assays (13). It appears for Tobias Acid, and for aryl amines in general, that the high solubility rendered by sulfonation results in rapid urinary clearance without metabolism. Despite this limited indication of toxicity, the British color industry recommended closed handling of Tobias Acid because of the risk of contamination with BNA (14). American Cyanimid, one of Ridgway's suppliers, evaluates this contamination as no more than 0.1% and on average 0.04%.

4. Beta Naphthol: Beta Naphthol and 3-hydroxy-2-naphthoic acid are widely used as intermediates in the synthesis of azo red colours. Red pigments numbered 48, 49, 53 and 57 (C.I.: 15865, 15630, 15585, 15850) utilize these intermediates at Ridgway Color. Although the disruption of azo linkages of ingested azo colours with subsequent absorption and metabolism could theoretically produce 1-naphthyl-2-hydroxyamine, a potent carcinogen in the rat, the low solubility of pigments should eliminate the hazard of this process and carcinogenic risk.

5. Toluidine Bases: Commercial preparations called C-amine, 4-B and 2-B acids (see Figure 1) are used as bases in the production of red pigments. Being highly substituted and sulfonated, they would not be expected to undergo metabolism in the body, based on observations with structurally similar chemicals(15). An important qualification, however, is that there has been no actual study of this group of toluidine bases, and that ortho and para toluidine, themselves, have had a demonstrated carcinogenic effect in animals (16,17,18).

6. Phthalocyanines: The phtalocyanine dyes have not been associated with tumour development in animals at high doses.

7. Hydrochloric Acid (HCL) or Muriatic Acid (38% Hydrogren Chloride):

HCL, hydrogen chloride, is a colorless, nonflammable gas, soluble in water. The aqueous solution is known as hydrochloric acid or muriatic acid and may contain as much as 38% HCI.

Local Effects - Hydrochloric acid and high concentration of hydrogen chloride gas are highly corrosive to eyes, skin, and mucous membranes. The acid may produce burns, ulceration, and scarring on skin and mucous membranes, and it may produce dermatitis on repeated exposure. Eye contact may result in reduced vision of blindness. Dental discoloration and erosion of exposed incisors occur on prolonged exposure to low concentrations. Ingestion may produce fatal effects from esophageal or gastric necrosis.

Systemic Effects - The irritant effect of vapors on the respiratory tract may produce laryngitis, glottal edema, bronchitis, pulmonary edema, and death.

VI. RESULTS AND DISCUSSION

A. Environmental (Refer to Table II)

The results of the DCB personal air sampling show no DCB detected for the work intervals sampled. The lower limit of detection is 1 ug/sample.

Results of the hydrogen chloride personal air sampling also showed none detected in the breathing zone of the operator; the lower limit of detection for HCI is 4 ug/sample.

And the results of the total dust personal air sampling show concentration values of 0.004 mg/M^3 for the dryer operator and 0.001 mg/M^3 for the blender and crusher operator.

Bulk samples of BONA, beta-Naphthol and Tobias Acid were analyzed for alpha and beta naphthylanine. The results showed none detected for either component in each bulk. The lower limit of detection id 0.04 mg of alpha/beta naphthylanine per gram of bulk.

Bulk samples of C-amine, 4-B Acid and 2-B Acid were analyzed for ortho and para toluidine. The results showed no ortho-toluidine detected in any of the bulks and no para-toluidine in the C-amine, 40 ug/gram of para-toluidine in the 4-B acid and 14 ug/gram of para-toluidine in the 2-B acid.

Although the odor/presence of hydrogen chloride was detected environmental measurements did not pick-up any significant amounts of the gas.

Assessment of ventilation systems showed the reaction and transfer vessels to be under negative pressure with a range of 100 to 250 feet per minute at the manway entrance. This is a satisfactory air velocity for these substances.

A local exhaust set-up on the "dumping out" operation was not effective in capturing the pigment dust, although air samples did not show any concentration in excess of the standards. Air velocity was measured as less than 50 feet per minute at the face of the exhaust located at the rim of the drum and zero at the center of the drum.

The local exhausts used in the salt grinding area were found to be greater than 100 feet per minute at the face of the enclosure, but some dust and mist (HCL) was observed to escape around this enclosure. Air samples showed hydrogen chloride levels to be non-detectable in this area.

Based on the air sampling and bulk analysis data, the substances evaluated by this study would not pose a potential health hazard to the chemical operators at this site.

However, recommendations concerning work practices, hygiene, clean-up procedures, and ventilation control to help improve the worker's environment are included in section VII.

B. <u>Medical</u>

1. Symptoms

The twenty-two production workers -- 18 day shift and 4 evening shift -- who where interviewed did not constitute a formally randomized sample of the work force, but the consistency of their symptoms obviated the need for a larger and systematic analysis. Their representativeness of the larger production work force is illustrated in Table III.

Table IV. presents principal symptoms of interest. Significantly the symptoms which occur, most frequently, among more than 25% of the work force, on a chronic basis involve mucosal tissue -- watery or itchy eyes, 59%; and runny nose or sneezing, 55%. The most frequently reported event -- pigmented nasal discharge in 95% of all responders -- suggests the likelihood of a significant inhalation and ingestion of pigment. Although the numbers are small, Table V. shows that these upper respiratory and mucosal complaints did not occur more frequently among smokers than among non-smokers. Because of the small sampe size and the inability of the environmental analysis to detect a gradient of exposure between work areas, there has been only a limited effort to identify symptoms with specific jobs. However as Table VI demonstrates, there was no significant difference in reported symptoms in a simple dichotomous comparison between presumably more chemically exposed workers (flushers, laborers, pressmen), and less chemically exposed workers (varnish makers, maintenance workers, tankmen).

Because of the concern over urinary tract cancer, questions about change in urinary habits over the past six months were included (Table VII). It is difficult to assign an interpretation to the two men reporting unusual frequency (more than 6x a day) or to the one man reporting an increase in frequency, withough a more substantial baseline. The absence of hematuria or dysuria conforms with the absence of hematuria or abnormal cytology on the semi-annual urine studies performed on Ridgway DCB workers. Although this type of screening may be of extremely low sensitivity in diagnosing early cancers or benign tumours of the bladder, in three years there have been no positive findings (19).

2. Epidemiological Mortality Study

Five workers were found to have died from cancer from the opening of the plant until a cut-off date of 12/31/81. Information on the duration of employment, and age at death and diagnosis, confirmed by physician and family are listed on Table VIII. Using United States age specific white male rates for all cancer (1970), these five cases compare with an expected occurrence of 3.92 cases of cancer (see Table IX.). The age adjusted overall United States cancer mortality rate of 185.1/100,000 (1970) is approximately 10% higher than the Elk County, Pennsylvania rate for 1950-69 (167.7/100,000). That is, all things being equal, a resident of Elk County would be expected to have a somewhat lower risk of dying from cancer than the national average.

Assessing the implications of the five known deaths is difficult, assuming even that some additional deaths may have gone uncounted. It would have required no less than nine documented deaths to achieve statistical significance at the .05 level (two-sided Poisson distribution), and as the power calculations in Table X. show, a relative risk of greater than 2.5 times (10 or more cases) is required to establish a statistical test of significant power. In summary, there is no direct evidence that Ridgway workers have a higher than normal risk of developing cancers, but because of the small number of people involved, it would require an exceptionally high rate of cancer to demonstrate an effect using statistical tests.

Although no cases of bladder cancer were observed, there was a single case of renal cancer among Ridgway workers. Renal cancer has been strongly associated with benzidine exposure, but not as strongly as has bladder cancer (19). Using the United States age adjusted white male rate (1970) for urinary tract cancers, 0.3224 cases would have been expected. It is impossible to conclude very much on the basis of one cancer death. However, given the low expected number of cases, there would have had to have been a ten-fold risk to appreciate a signficant statistical increase in bladder cancer cases among the small number studied (Table XI.).

It may be argued that insufficient time has passed to fully estimate the risk of developing bladder cancer. Experience with benzidine and BNA have shown that urinary bladder tumours, which occur most commonly after the sixth decade of life in the general population, occur much earlier in industrial workers exposed to these bladder carcinogens. A latency of 16-18 years is the average time from exposure to development of tumour, but with a range that extends from 1-45 years (1,14). An analagous estimate of latency for DCB exposure, the principal source of concern at Ridgway, is not available because workers who have been exposed to DCB and no other carcinogen constitute too small a group for generating an estimate. But the above numbers are a rough guide and sufficient time should have passed to observe an effect, provided it were strong.

3. DCB Assay

Urine samples from nineteen production personnel and two non-exposed controls were analyzed for the presence of DCB. Analysis was by electron capture gas chromotography (EC-GC) with a sensitivity of 10 ug/ml. There was no DCB detectable. The procedure for this analytical technique is documented in Appendix I.

VII. RECOMMENDATIONS

1. Although environmental measurements showed all substances tested to be below the permissible exposure limit, ventilation in the dumping out area and in the salt grinding area should be improved through increased capture velocity and an effective enclosure design. This would address the chronic respiratory irritation noted on employee questionnaires.

Periodic checks and maintenance of the new and old ventilation systems whould be done in a diligent and comprehensive manner to assure proper performance of these units.

2. All respirators should be stored in a clean storage box/area when not in use. The throw away paper masks should be tossed out after they have been used and not to be kept for use the next day.

3. Operators who come in contact with the start-up chemicals or the pigment should wash up before break-time, lunch and before going home; this will prevent any skin absorption or damage, ingestion or respiration of any possibly toxic materials.

4. Although there appears to be no cancer excess at this time, there may be significant problems of underreporting, because any errors in the determination of cancer cases would be in the failure to recognize a case. Therefore, NIOSH recommends that the Ridgway personnel department maintain death certificate copies or a comparable type of record of all deaths among active, former or retired employees. In the event of a single additional death from bladder or renal cancer, NIOSH should be notified. If over a ten-year period, more than one-third of all deaths are due to cancer, this situation should be reported.

5. The handling of imported chemical intermediates without documentation of toxicity by material safety data sheets poses a potential hazard. Although, NIOSH did not detect a hazardous level of contaminant carcinogens in bulk samples, this single assay does not confer adequate security. Without information on quality control and trace contamination, there is a possibility of serious exposure to known carcinogens.

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X. AUTHORSHIP AND ACKNOWLEDGEMENTS

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XI. DISTRIBUTION AND AVAILABILITY OF REPORT

Copies of this report are currently available upon request from NIOSH, Division of Standards Development and Technology Transfer, 4676 Columbia Parkway, Cincinnati, Ohio 45226. After 90 days, the report will be available through the National Technical Information Service (NTIS), 5285 Port Royal, Springfield, Virginia 22161. 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. Russ Francis, Plant Manager, Ridgway Color
2. Forrest Kinley, Secretary, USWA, Local 1694
3. NIOSH, Region III
4. OSHA, Region III

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.

TABLE I

HETA 81-399

Ridgway Color Company
Ridgway, Pennsylvania

Evaluation Criteria
permissible Exposure Limits

Substances	NIOSH	OSHA	ACGIH
3,3'-Dichlorobenzidine	-	-	No exposure by any route should be permitted*
Hydrogen Chloride	-	5 ppm-ceiling**	5 ppm-ceiling***
Total Dust, Gravimetric (Barium Lithol Pigment)	-	15 mg/M^3-TWA***	10 mg/M^3-TWA***

* Industrial Substances Suspect of Carcinogenic Potential for Man.

** Ceiling Values = Not to exceed this value; OSHA requires 15 min. sampling period.

*** TWA = Time Weighted Average (8-hrs.)

TABLE II

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Ridgway Color Company
Ridgway, Pennsylvania

Air Sampling Results for December 17, 1981

Substances	Location/Operation	Sampling Time	Concentration
3,3'-Dichlorobenaidine	Tank floor Operation (6 drums emptied)	10 min.	N.D. *
	Tank Floor Operation Drum Taansfer (6 drums)	18 min.	N.D. *
	Drum Emptying (6 drums)	10 min.	N.D. *
Hydrogen Chloride	Tank Floor Operation Rubin Red Operation	450 min.	N.D. *
	Tank floor Operation Barium Lithol Operation (new unit)	430 min.	N.D. *
	Tank Floor Operation Barium Lithol Operation (old unit)	400 min.	N.D. *
	Tank Floor Operation Salt Grinding Operation	60 min.	N.D.*
Total Dust, Gravimetric (Barium Lithol Pigment)	Dryer Operation Dumping out Operation	475 min.	0.004 mg/M^3 - TWA**
	Blender & Crushing Operation	478 min.	0.001 mg/M^3 - TWA**

* N.D. = None Detected

** TWA = Time Weighed Average (Based on 8=hr. exposure)

TABLE III -- Profile of Plant Workforce and Study Group Stratified by Age and Work Area

Age	Study Group	Plant Population
20-29	8	30
30-39	8	18
40-49	1	17
50-59	4	19
60-65	1	10
	22	94

Job Title	Study group (day shift)	Plant (day shift)
Flusher	6	8
Labor Pool	3	8
Varnish	2	3
Tankmen	2	3
Maintenance	3	12
Pressmen	2	4
Total	18	38 (excluding lab workers)

TABLE IV

Symptoms List

Symptom	At least x1 in past year	At least x5 in past year
Watery,itchy eyes	15 (68%)	13 (59%)
Nosebleeds	2 (09%)	1 (05%)
Pigmented nasal discharge	21 (96%)	21 (96%)
Runny nose, sneezing	14 (64%)	12 (55%)
Skin rash	7 (32%)	4 (18%)
Coughing Spells	8 (36%)	5 (23%)
Coughing with phlegm	7 (32%)	4 (18%)
Wheezing	6 (27%)	4 (18%)
Shortness of Breath	6 (27%)	5 (23%)
Loss of balance/dizziness	2 (09%)	5 (23%)

TABLE V

Irritant complaints among study group analyzed by plant location.

Symptom	Exposed Area*	Less Exposed Area**	P-value
Eye irritation	9/13	5/9	N.S.
Nasal symptoms	7/13	5/9	N.S.

(Statistical test is Fisher's Exact)

* More exposed = Flushers, Labor Pool, Pressmen

** Less Exposed = Varnish Operators, Tankmen, Maintenance

TABLE VI

Irritant complaints controlled for smoking among study population supplying a smoking history.

Symptom	Current smoker	Non or former smoker	P-value
Cough	1/7	4/15	N.S.*
Watery or itchy eyes	3/7	10/15	N.S.*
Runny Nose	4/7	8/15	N.S.*

(Fisher's Exact Test)

N.S. = Not statistically significant.

TABLE VII

Urinary tract symptoms
(change over last 6 months)

Responders	22
Increased frequency	2
Pain	0
Loss of control	0
Burning	0
Blood or clots	0
Nocturia (more than twice)	3
Polyuria (more than 6x/day)	2

TABLE VIII

Case #	Year of Death	Age at Death	Years at Job	Cause of Death
1.	1973	69	26	Metastatic carcinoma
2.	1973	65	10	Bronchogenic carcinoma
3.	1974	58	07	Gunshot wound
4.	1975	69	11	Obstructive lung disease
5.	1976	70	19	Hypernephroma
6.	1978	70	20	Myocardial infarction
7.	1979	58	23	Myocardial infarction
8.	1979	53	23	Esophageal cancer
9.	1980	63	22	Myocardial infarction
10.	1980	65	13	Bronchogenic carcinoma

(List includes all deaths occurring through 12/31/81)

TABLE IX

Calculation of Person Years at Risk

Sample size = 30
Population = 139
Sample ratio = 4.63

Age Group by Years	18-34	35-49	50-64	>65
Person Years -- sample	75	134	129	16
Person Years -- population	347.25	620.42	597.27	74.08

TABLE X

Power calculations -- all cancers

Age Group	18-34	35-49	50-64	>65
Deaths/100,000	50.1	90.7	389.5	1154.0
Expected Deaths	.174	.563	2.326	.855

Total expected deaths: (E) = 3.92

Relative Risk	P (power)
2.0	.50
2.5	.74
3.0	.90

USA white male rates (1970)

TABLE XI

Power calculations -- Urinary tract cancers

Age Group	18-34	35-49	50-64	>65
Deaths/100,000	.233	3.23	21.37	234.9
Expected Deaths	.0008	.0200	.1276	.1740

Total Expected Deaths: (E) = .3224

Relative Risk	P value (power)
2	.12
5	.40
10	.74

Appendix 1

Twenty urine specimens were collected from employees of Ridgway Colors, Ridgway, Pennsylvania. The employees were possibly exposed to diarylanilide pigments which might be metabolized in humans to the suspected human carcinogen, 3,3'-dichlorobenzidine (DCB). The urine samples were received in December, 1981 by the Clinical and Biochemical Support Section (CBSS) and kept frozen until analyses in February.

Four ten-ml-urine-aliquots were analyzed for DCB from each sample. Two aliquots were analyzed for total DCB (conjugated and free) and two were analyzed for free DCB. Only free DCB was determined for sample 14 since the sample volume was less than 25 ml. Glucose was determined by dipping Bililabstix into each urine. Ninety-eight individual analyses were performed.

The procedure utilized for DCB determinations was developed by Nony and Bowman[1] with three modifications: (1) a hydrolysis with 10-ml of 10 normal sodium hydroxide at $85^{0}C$ for two hours was performed to release DCB from possible metabloic conjugates; (2) a florisil column cleanup of the urine-benzene extract after heptaflurobutyric anhydride derivitization was performed to remove interferences by benzene extractables; and (3) a 15-meter-SE-54-capillary-gas chromatographic column was used for analyses. The detection limit was calculated utilizing information presented by Nony and Bowman[1] and florisil column recovery studies conducted by the clinical and Biochemical Support Section (CBSS). Recoveries averaged 72% for the procedure. The percent recovery was determined by spiking DCB free urine with DCB until the urine DCB concentrations were 20, 100 and 200 ng DCB/ml urine. The spiked urines were analyzed for DCB using the above outlined procedure. All sample urines had DCB concentrations below the estimated detection limit of 10 ng DCB/ml urine. All urine glucose values were negative as determined by Bililabstix. However, considering the age of the sample, approximately two months, this value may not reflect actual glucose values at the time of sample collection.

Two chromatograms are attached. They illustrate representative chromatograms of a standard and a sample. They show the procedure is sensitive with excellent resolution of DCB from other compounds in a complex chromatogram.

Reference:

1. Nony, Charles A., Bowman, Malcolm C., Trace Analysis of Potentially Carcinogenic Metabolites of an Azo Dye and Pigment in Hamster and Human Urine as Determined by two Chromatographic Procedures, Journal of Chromatographic Science, Vol. 18, pages 64-74, February, 1980.

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