

INDUSTRYWIDE STUDIES REPORT OF  
INDUSTRIAL HYGIENE SURVEYS AT THE

CIBA-GEIGY CORPORATION  
Toms River Chemical Plant  
P.O. Box 71  
Toms River, New Jersey 08754

SURVEYS CONDUCTED BY:  
Bruce Hills

DATE OF SURVEYS:  
August 12-13, 1985  
September 25-27, 1985  
November 7, 15, 1985

REPORT WRITTEN BY:  
Bruce Hills

DATE OF REPORT:  
May, 1987

REPORT NUMBER:  
93.26

Industrial Hygiene Section  
Industrywide Studies Branch  
Division of Surveillance, Hazard Evaluations and Field Studies  
National Institute for Occupational Safety and Health  
Centers for Disease Control  
Cincinnati, Ohio



<b>REPORT DOCUMENTATION PAGE</b>	1. REPORT NO.	2.	3. Recipient's Accession No. <b>PBB7 2225847AS</b>
4. Title and Subtitle Industrywide Studies Report of Industrial Hygiene Surveys at the CIBA-Geigy Corporation, Toms River Chemical Plant, Toms River, New Jersey, Report No. IWS-093-26		5. Report Date 8/7/05/00	
7. Author(s) Hills, B.		8. Performing Organization Rept. No. IWS-093-26	
9. Performing Organization Name and Address Division of Surveillance, Hazard Evaluations and Field Studies, NIOSH, U.S. Department of Health and Human Services, Cincinnati, Ohio		10. Project/Task/Work Unit No.  11. Contract(C) or Grant(G) No. (C) (G)	
12. Sponsoring Organization Name and Address		13. Type of Report & Period Covered  14.	
15. Supplementary Notes			
16. Abstract (Limit: 200 words) <p>Personal and area samples were collected at each step during the production of a dye batch, except during the removal of the wet cake from the filter press, at the CIBA-Geigy Corporation (SIC-2865) located in Toms River, New Jersey. All personal monitoring was conducted for o-dianisidine (119904) dyes, and the area monitoring was performed for o-dianisidine dyes and total dust. Airborne total dye concentrations as high as 1.64mg/m<sup>3</sup> were generated during the processing of dry dye. However, these were brief excursions occurring adjacent to the process equipment. The operators were required to wear respiratory protection while handling the dye. Air concentrations of dye at work stations next to the blending and grinding of the dye were below 0.24mg/kg. These operators also wore respiratory protection. The unreacted or free o-dianisidine in the dye C.I.-Direct-Black-91 (59537450) being processed during the survey was about 11 parts per million. The author recommends that biological monitoring be performed on the workers to obtain more accurate exposure data. Biological monitoring of urine would detect the metabolite of benzidine congener dyes.</p>			
17. Document Analysis a. Descriptors  b. Identifiers/Open-Ended Terms NIOSH-Publication, NIOSH-Author, NIOSH-Survey, Field-Study, IWS-093-26, Region-2, Chemical-manufacturing-industry, Dyeing-industry, Azo-compounds, Carcinogens, Dust-inhalation  c. COSATI Field/Group			
18. Availability Statement		19. Security Class (This Report)	21. No. of Pages 17
		20. Security Class (This Page)	22. Price

DISCLAIMER

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

**PURPOSE OF SURVEY:**

To conduct an industrial hygiene survey of a dye manufacturer as part of the o-Dianisidine and o-Tolidine Dye Workers Exposure Study.

**EMPLOYER REPRESENTATIVES**

**CONTACTED:**

Louis Ortiz; Director of Safety and Industrial Hygiene  
Paul Hutter; Industrial Hygienist  
Martin E. Bernstein; Manager, Toxicology Safety, Health & Ecology  
Douglas J. Hefferin; Attorney  
Charles Motta; Manager Azo Dye Production: Oil  
Per S. Stensby, Ph.D., Executive Director, Safety & Environmental Affairs

**EMPLOYEE REPRESENTATIVES**

**CONTACTED:**

George Wooley; Safety Representative:  
Oil, Chemical & Atomic Workers International Union, AFL-CIO

**STANDARD INDUSTRIAL**

**CLASSIFICATION (SIC):**

2865 - Industrial Organic Chemicals; Cyclic (Coal Tar) Crudes, and Cyclic Intermediates, Dyes, and Organic Pigments (Lakes and Toners)

## ABSTRACT

Four industrial hygiene surveys were conducted at the Ciba-Geigy plant in Toms River, New Jersey. This Ciba-Geigy facility is a major producer of o-dianisidine and o-tolidine based dyes. Three of the four surveys involved monitoring workers exposure to the dyes. The surveys were conducted to assess exposure to the o-dianisidine based dye, C.I. Direct Black 91. The separate surveys were necessary because the dye was processed on three different occasions. The indepth surveys were completed during the production of an o-dianisidine based dye including tetrazotization and coupling of o-dianisidine dihydrochloride to form the dye and ending with the packaging of the dye product. Seven workers were observed handling the dye and dye intermediates. There were several other workers who were in the vicinity of production for short periods of time but their exposure was minimal. Overall, eight employees were observed to be involved in the production of the dye. The personal air monitoring results obtained outside the respirators worn by the employees ranged from non-detectable to 1.64 mg total dye/m<sup>3</sup>. The area air monitoring levels ranged from non-detectable to 0.38 mg total dye/m<sup>3</sup>. Employee exposures to the dye were probably below the above levels because all employees wore respirators while processing the dye and dye intermediates. A recommendation was made to further insure that the dye workers are not being exposed to benzidine congener dyes. Another recommendation was that the company should consider instituting a screening of employees' urine for dye metabolites.

## INTRODUCTION

Many synthetic organic dye stuffs contain benzidine, a regulated carcinogen, or congeners of benzidine such as o-tolidine (3,3'-dimethylbenzidine) and o-dianisidine (3,3'-dimethoxybenzidine). The benzidine-based dyes contain benzidine attached, or coupled, to other chemical substituents by azo linkages. Likewise, dyes based on o-tolidine and o-dianisidine use this same azo bond to link to other substituents.

Benzidine is linked to bladder cancer in humans while o-tolidine, o-dianisidine, and 3 benzidine based dyes have been shown to be carcinogenic in animal studies (1-3). Because o-tolidine and o-dianisidine are structurally similar to benzidine, there is concern that all benzidine congener dyes may be carcinogenic.

Benzidine based dyes, as well as o-tolidine and o-dianisidine based dyes can be metabolically reduced in vivo to their parent aromatic amines. Several studies (4-6) have demonstrated a severing of the diazo linkage in the dyes by intestinal microflora and to some extent by hepatic (liver) microsomal enzymes. Free benzidine and monoacetyl benzidine have been found in the urine of Rhesus monkeys fed benzidine based dyes containing no detectable free benzidine (7). Other studies on animals have shown that dyes made from o-tolidine and many dyes made from o-dianisidine are also metabolized to their parent compounds (8-11).

Besides the biological reduction of the diazo dyes, the azo bond can also be broken by chemical and/or physical means (12-14) which may result in a direct exposure to benzidine congeners.

In a recent study, researchers dosed rabbits with a radioactive labeled benzidine based dye (C.I. Direct Black 38) by cutaneous application. The investigators reported that cumulative excretion of labeled benzidine was 3.12% of total dermal dose in the urine and 5.12% of total dermal dose in the feces (15). Apparently, either the dye molecule was being absorbed through the skin or the diazo linkage was being severed on the surface of the skin liberating benzidine.

Research performed by NIOSH investigators has supported those observations by detecting free benzidine in the urine of workers who were exposed to benzidine-based dyes (14,16). NIOSH and OSHA have concluded that, "benzidine-based dyes are potential human carcinogens" (17). Because of possible health risks to workers, dyes made from benzidine congeners, namely o-tolidine (3,3'-dimethylbenzidine) and o-dianisidine (3,3'-dimethoxybenzidine) have been chosen by NIOSH researchers for further study. The purpose of this survey is to determine if workers are being exposed to airborne concentrations of o-dianisidine based dye during production of the dye. The information obtained from this survey along with other survey data will be used for future assessments of the health risks to workers who are exposed to benzidine congener dyes.

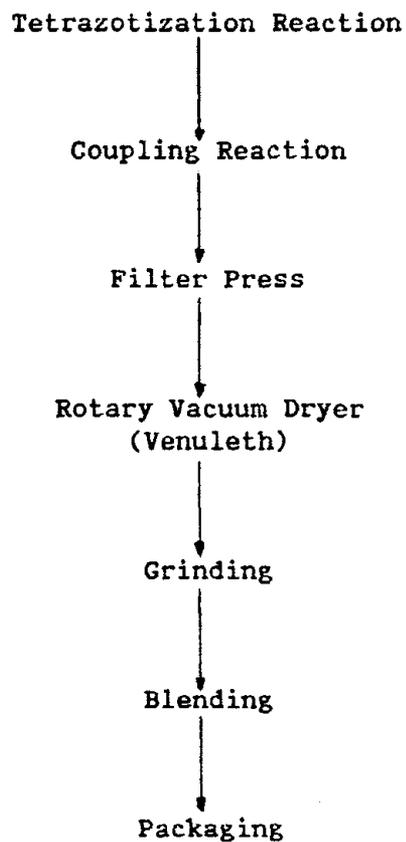
## PLANT AND PROCESS DESCRIPTION

The entire plant occupies approximately 1,300 acres. The active production buildings occupies approximately 3 acres. Dye production occurs in two buildings: the azo production building where the dyes are synthesized, and the standardization building where the dyes are adjusted to a desired strength. Production of anthraquinone dyes began in the azo building in 1952 and ended in 1983. The production of azo and vat dyes began in 1960 and still continues. The company also manufactures resins and plastics in separate buildings.

It is typical procedure in dye manufacturing to extend the production of a single dye batch over several months to allow for efficient scheduling of personnel. Inventory and customers orders can also affect the time period for a particular dye batch. The production of C.I. Direct Black 91 (an o-dianisidine based dye) began on September 26. Currently, there are 24 batches of Direct Black 91 made during the year.

Production began in the azo production building where the dye is synthesized by a tetrazotization and coupling reaction of o-dianisidine dihydrochloride (Figure 1). First drums of dry o-dianisidine dihydrochloride were poured into the top of a 30 foot reactor vessel by two chemical operators with the aid of a forklift. Pouring of the o-dianisidine dihydrochloride lasted for 20 minutes. The top of the reactor vessel or kettle is on the third floor. Water, ice, hydrogen chloride as muriatic acid, sodium nitrite, ammonia sulfamate, and sodium carbonate were then added to the reactor. After the tetrazotization reaction was completed and excess nitrite was removed, the contents were pumped into a second reactor kettle where the coupling components were added: first salicylic acid and then cuprophenyl intermediate. The product was transferred again to third kettle and caustic soda was added followed by glacial acetic acid. Moisture was removed from the final product on an filter press on the second floor. After separation, the dye has the consistency of a wet paste. Two workers using metal scrapers removed the paste from the press in approximately 2 hours. The paste then dried in a rotary vacuum dryer known as the Venuleth on the first floor. The dye was dried for 20 to 30 hours at temperatures below 300°F. Once drying was complete, the dye was "discharged" into 55 gallon drums by a chemical operator. This was accomplished by allowing the dye to fall into drums below the Venuleth. A cloth-metal cover was used between the Venuleth and the drum to prevent the escape of dye dust. When the cloth-metal cover was removed prior to replacement with a metal drum lid, airborne dye can escape into the work area. The airborne dye was visible in the vicinity of the Venuleth. This step requiring 20 minutes to complete was the dustiest operation of dye production. Approximately a ton of dry dye was produced at this stage. After the discharge, the dye was sent to the standardization building and set aside for 41 days until November 7.

FIGURE 1  
PROCESS FLOW FOR THE PRODUCTION  
OF C.I. DIRECT BLACK 91  
CIBA-GEIGY CORPORATION



Once in the standardization building, the concentration of the final dye product is adjusted. Since the dye strength varies from batch to batch, the amount of standardizing agents (salts and dextrin) used to adjust dye strength will also vary. Standardization is usually accomplished by adding about 8.0% (on weight of final product) of standardizing agents.

During the survey on November 7, the dye was loaded into the blender/pulverizer by dumping the dye from drums into the top of the tank on the third floor by one employee. Local exhaust ventilation surrounds the opening of the blender/pulverizer. The standardizing agents were then added to the dye to reduce the concentration. After blending/pulverizing the dye was removed from the blender/pulverizer on the first floor by a method similar to discharging the Venuleth. A cloth-metal cover directed the dye into the drums. The difference is that this equipment has local exhaust ventilation attached at the base of the cloth-metal cover where as the Venuleth had no such ventilation. The grinding-blending step was performed by two chemical operators over 2 shifts. On November 15, 1985 the dye was blended with a dedusting agent by two operators. The final dye product was then dumped into polyethylene bags for export shipment and fiber drums for domestic customers.

After each step in dye production the worker washed the equipment and floors with a water hose. Metal drums used for storing and transporting the dyes are washed for recycling by a robot.

Six other dyes derived from o-tolidine or o-dianisidine have also been produced at this plant during the last two years.

#### DESCRIPTION OF WORKFORCE

The plant operates 7 days a week utilizing 4 work shifts. Employees work 7 days then have 2 days off followed by 7 more work days and 3 days off. The azo production building has 162 employees, 117 of whom are laborers and chemical operators. The standardization building has 14 employees, including 10 chemical operators that work 2 shifts. The chemical operators and laborers are responsible for each step in production and may process several different dyes during one shift. A typical number of operators required to produce one batch of a dye is 8. If a particular step in the process should extend into another shift then additional employees will handle the dye. During the production of the Direct Black 91 batch during the NIOSH surveys, 8 separate workers were directly involved in the production. Since an operator may process many different dyes, it is possible that nearly all production employees will handle a benzidine congener dye at least once per year.

#### DESCRIPTION OF MEDICAL, INDUSTRIAL HYGIENE AND SAFETY PROGRAMS

The company has a medical staff at the corporate offices and at the Toms River plant. The on site medical staff includes two part time physicians,

two full time nurses, and a medical technician. A hospital is located four miles from the plant. Employees are provided with pre-employment and annual physicals. The physicals include X-rays, blood tests, urine tests, EKG, hearing, eye, and pulmonary testing.

The industrial hygiene and safety department is staffed by 2 industrial hygienists and a safety professional. This group provides extensive occupational health and safety training programs to employees. Meetings are held weekly with the employees to discuss potential health or safety problems in the plant. The union representative responsible for safety is kept informed of these discussions. The industrial hygiene department also performs the respirator fit testing of employees.

Employees are required to wear hard hats, safety shoes, safety glasses, and coveralls. Dust masks (NIOSH approval number TC-21C-132) are required when handling dry dyes and a NIOSH approved half-face respirator with cartridges for dusts and vapors when handling o-dianisidine. The company has an agreement with the union that employees are not permitted to have facial hair that would interfere with the effectiveness of a respirator.

#### DESCRIPTION OF PAST EXPOSURES

The company's method for monitoring dye exposures is to collect personal and area samples for total dust. These monitoring data were not collected during the survey.

#### DESCRIPTION OF SAMPLING AND ANALYTICAL METHODS

##### Sampling Strategy

The sampling strategy was to collect personal and area samples at each step in the production of a dye batch except for the removal of the wet cake from the filter press. Particulate material is not generated during this step. Since the production of Direct Black 91 was not continuous, the surveys were conducted on 3 separate occasions. All personal monitoring was conducted for o-dianisidine dyes and the area monitoring was performed for o-dianisidine dyes and total dust. Monitoring was performed on all individuals who handled the dye except for the workers who scraped the wet dye paste from the filter press.

##### Sampling and Analytical Methods

The sampling for total dust was conducted by the NIOSH method 0500. Samples were collected on 37-mm, polyvinyl chloride filters with a 5-um pore size membrane inside a closed face cassette filter holder. The sampling pumps were calibrated before and after the survey at a flow rate of 1.7 liters of air per minute. The filters were pre-weighed at Utah Biological Testing Laboratory (UBTL) and weighed by UBTL after sampling. The range of the method is 0.3 to 2 mg per sample and the limit of detection is 0.2 mg per sample.

O-dianisidine dyes were analyzed for o-dianisidine by the NIOSH method 5013. Samples were collected on 37-mm, Teflon (PTFE) membrane filters with a 5-um pore size membrane inside a cassette filter holder. The sampling pumps were calibrated before and after the survey at a flow rate of 3.0 liter of air per minute. The samples were desorbed with water and analyzed at UBTL by reductive cleavage of the dye to the free o-dianisidine with sodium hydrosulfite. The samples were then injected into a high performance liquid chromatograph with an ultra-violet detector (HPLC UV). The method has a range of 15 to 250 micrograms (ug) per sample and a limit of detection of 3 ug per sample. The laboratory results are reported in quantity of o-dianisidine per sample. From this value the amount of pure dye can be calculated from the molecular weight of the o-dianisidine and the dye. The Direct Black 91 contains 26.46% o-dianisidine chemically bound within the dye molecule. Since dyes are never 100 percent pure, but contain salts, dextrin, mineral oils, and water, the concentration of pure Direct Black 91 was determined by HPLC.

The Direct Black 91 or "total dye" (containing pure dye plus additives) was analyzed for unreacted or free o-dianisidine by dissolving 50 mg of the dye in 30 ml of 0.12 N NaOH. Five ml of chloroform was used to extract the o-dianisidine by shaking for 30 minutes. The chloroform and aqueous layers were separated using a centrifuge and the aqueous layer was pipetted off. After recording the volume of remaining chloroform, it was passed through sodium sulfate and placed in an evaporator tube where it was dried in a hot water bath under a stream of nitrogen. The remaining residue was brought up with 500 ul of methanol, sonicated for 20 minutes, and filtered through a 0.45 micron nylon filter. The sample was then analyzed using HPLC with a UV detector. The limit of detection was 4 ug/g and the limit of quantitation was 11 ug/g.

#### APPLICABLE STANDARDS AND RECOMMENDED LIMITS

NIOSH recommends that employers reduce workplace exposure to dyes based on benzidine, o-dianisidine, or o-tolidine to the lowest feasible level or replace these dyes with less toxic dyes (18).

The Occupational Safety and Health Administration (OSHA) currently does not have exposure standards for the benzidine congener dyes. However, OSHA had established the Hazard Communication Standard which requires that employers transmit to their employees any information concerning the hazardous properties of chemicals in their work environment (19). This is to be accomplished by labeling containers, providing material safety data sheets to workers, and training programs for workers. In addition, it is the responsibility of chemical manufacturers and importers to assess the hazards of the dyes which they produce or import. OSHA considers, "evidence which is statistically significant and which is based on at least one positive study conducted in accordance with established scientific principles is considered to be sufficient to establish a hazardous effect if the results of the study meet the definition of health hazards in this section." The applicable section is Appendix A and B of CFR 1910.1200.

Compounds that have been reported to be animal carcinogens are benzidine, o-dianisidine, o-tolidine, and the benzidine based dyes; Direct Blue 6, Direct Black 38, and Direct Brown 95 (20). The National Toxicology Program is currently conducting toxicologic and carcinogenesis bioassays on benzidine, o-dianisidine, o-tolidine, Direct Blue 6 (benzidine based), Direct Blue 15 (o-dianisidine based), Direct Blue 218 (o-dianisidine based), and Acid Red 114 (o-tolidine based). The results of this study are expected in 1987. Since the testing of each benzidine congener dye in a standard bioassay would require an enormous amount of time and expense, and the fact these dyes are reduced back to benzidine and its congeners in the body, OSHA may soon consider all benzidine congener dyes as hazardous materials. At this time, the benzidine congener dyes which are complexed to a metal are not known to be carcinogenic.

The American Conference of Governmental Industrial Hygienists (ACGIH) recommends that exposure to nuisance particulates (dust) be no greater than 10 mg/m<sup>3</sup> of total dust that contains less than 1% quartz. The recommended standard for respirable dust is 5 mg/m<sup>3</sup> (21). The OSHA standard for inert or nuisance dust is 15 mg/m<sup>3</sup> for the respirable fraction provided the dust contains less than 1% quartz (22).

#### DISCUSSION OF SAMPLING RESULTS

Analyses of the bulk dye samples, collected after Venuleth drying and blending, for free or unreacted o-dianisidine showed the dye to contain no greater than 11 ug o-dianisidine per gram of total dye. Incomplete dye synthesis is probably the most likely source of this residual o-dianisidine.

The analyses for the purity of the total dye revealed that it is composed of approximately 14% o-dianisidine. Since o-dianisidine makes up 26.46% of pure C.I. Direct Black 91, based on the molecular weights of the compounds, the concentration of pure C.I. Direct Black 91 can be calculated by multiplying the amount of o-dianisidine by 3.78. Since the pure C.I. Direct Black 91 makes up approximately 52.9% of the total dye, the quantity of total dye can be calculated by multiplying pure dye by 1.89. These total airborne dye concentrations are only approximations because the ratio of non-colorant materials to pure dye may differ between the bulk dye samples and the filter samples. The adjustments are necessary in order to compare our dye monitoring data with past air sampling of dyes where only total dust levels were measured.

The air monitoring results are listed in Tables 1, 2, and 3. Monitoring began with the two workers who loaded the o-dianisidine into the reactor kettle. Loading lasted for 23 minutes and both workers wore rubber gloves and MSA Comfo II, GMC Type, respirators. One respirator had a cartridge for gases and vapors but no cartridge for dusts or mists. Personal exposure and area air concentration samples collected during the loading of dry o-dianisidine were all non-detectable for o-dianisidine.

The discharging of the Venuleth by the operator took 32 minutes. The operator then spend 12 minutes moving the drums and sawing the area with a water hose. The operator wore a dust mask, rubber gloves, safety glasses, hard hat, and coveralls. The personal exposure monitoring during the Venuleth discharging showed airborne dye levels of 0.87 mg pure dye/m<sup>3</sup> or 1.64 mg total dye/m<sup>3</sup> for 32 minute sampling period. The area air monitoring samples ranged from non-detectable to 0.20 mg pure dye/m<sup>3</sup> or 0.38 mg total dye/m<sup>3</sup> at a location 30 feet from the Venuleth. There were no other workers in the vicinity of the Venuleth.

The grinding and blending of the dye on November 7 and 15 took place in the standardization building. Four operators were responsible for this step and exposure times ranged from 40 to 199 minutes. The workmen wore dust masks during this period. Several other workers were in the area but they remained for less than 20 minutes. Personal exposure samples during the grinding and blending ranged from non-detectable to 0.25 mg pure dye/m<sup>3</sup> or 0.47 mg total dye/m<sup>3</sup>. The area air monitoring samples which were placed 10 to 30 feet from workers ranged from non-detectable to 0.12 mg pure dye/m<sup>3</sup> or 0.23 mg total dye/m<sup>3</sup>. Total nuisance dust measurements ranged from 0.16 mg/m<sup>3</sup> to 0.17 mg/m<sup>3</sup>. It should be noted that all employees wore a dust mask when working with the dry dye.

#### CONCLUSIONS

Based upon the observations of this survey and other industry contacts, dye production is not a continuous process but very sporadic. One batch of a dye may take several months to complete and the scheduling is often done on the day before production is to begin. Although typically only 8 workers are needed to manufacture a dye batch, workers are often rotated to different tasks and a larger number of workers will come in contact with the benzidine congener dyes on an infrequent basis. Each step in dye production usually takes less than 5 hours to complete. Airborne total dye concentrations as high as 1.64 mg/m<sup>3</sup> are generated during the processing of dry dye. However, these are brief excursions occurring adjacent to the process equipment. Since the operators must wear respiratory protection while handling the dye, their exposure to the dye is assumed to be less than if no respirator is worn.

In the standardization building, production employees are working in the same room where the o-dianisidine based dye is being processed. Air concentrations of dye at work stations next to the blending and grinding of the dye are below 0.24 mg total dye/m<sup>3</sup>. Likewise, these operators wear respiratory protection which will reduce exposure to the dye.

The unreacted or free o-dianisidine in the dye C.I. Direct Black 91 being processed during this survey was approximately 11 ppm.

The industrial hygiene group at the company has made improvements in controlling exposures to hazardous substances. The company also has "state of the art" production equipment to prevent the loss of materials and to prevent exposures.

## RECOMMENDATIONS

Since personal air monitoring of workers who are wearing respirators can only give a rough approximation of actual exposures, it is advisable to perform biological monitoring of these workers to obtain more accurate exposure data. The company's medical and industrial hygiene departments should consider using biological monitoring of employees urine to detect the metabolite of benzidine congener dyes. Two methods have been developed by NIOSH, methods 8304 and 8306 which can be used to analyze for o-dianisidine (23,24).

## REFERENCES

1. Textile Chemist and Colorist. Buyer's Guide. American Association of Textile Chemists and Colorists, Research Triangle Park, NC 16(7), 74-80, 1984.
2. IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man. International Agency for Research on Cancer. Lyon, France, 4, 41-47, 1974.
3. IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man. International Agency for Research on Cancer. Lyon, France, 1, 87-91, 1972.
4. NCI Report 1358: 13 week subchronic toxicity studies of Direct Blue 6, Direct Black 38, and Direct Brown 95 dyes, NCI-CG-TR-108, DHEW Publication No. (NIH) 78-1358. US Department of Health, Education, and Welfare, Public Health Service, National Institutes of Health, National Cancer Institute, 127 1978.
5. Hartman, C., Fulk, G., and Andrews, A.; Azo reduction of Trypan Blue to a known carcinogen by a cell-free extract of a human intestinal anaerobe. Mut Res 58, 125-132, 1978.
6. Martin, C., and Kennelly, J.; Rat liver microsomal azoreductase activity for four azo dyes derived from benzidine 3,3'-dimethylbenzidine or 3,3'-dimethoxybenzidine. Carcinogenesis 2(4) 307-312, 1981.
7. Roxon, J, Ryan, A., Wright, S.; Reduction of water-soluble azo dyes by intestinal bacteria. Food Cosmet Toxicol 5, 367-369, 1967.
8. Rinde, E. and Troll, W.; Metabolic reduction of benzidine azo dyes to benzidine in the Rhesus monkey. JNCI 55(1), 181-182, 1975.
9. Lynn, R., Donielson, D., Ilian, A., Work, K., Kennish, J., and Mathew, H.; Metabolism of biasobiphenyl dyes derived from benzidine, 3,3'-dimethylbenzidine or 3,3'-dimethoxybenzidine to carcinogenic aromatic amines in the dog and rat. Toxicol Appl Pharm 56, 248-258, 1980.
10. Bowman, M. C. et al; Metabolism of nine benzidine-congener-based azo dyes in rats based on gas chromatographic assays of the urine for potentially carcinogenic metabolites. J Anal Toxicol 7(1), 55-60, 1983.
11. Nony, C. R. et al.; Chromatographic assays for traces of potentially carcinogenic metabolites of two azo dyes, Direct Red 2 and Direct Blue 15, in rat, hamster and human urine. J Anal Toxicol 7(1), 40-80, 1983.
12. Nony, C., Bowman, M., Cairns, T., Lowry, L. and Tolos, W.; Metabolism studies of an azo dye pigment in the hamster based on analysis of the urine for potentially carcinogenic aromatic amine metabolite. J Analy Toxicol 4, 132-140, 1980.

13. Melnikov, B., Kirillova, M.; Thermal stability of direct dyes in solution. J Appl Chem USSR (Eng Transl) 42(11), 2418-2422, 1969.
14. Aldrich, F.D., Busby, W.F. and J.G. Fox. Excretion of radioactivity from rats and rabbits following cutaneous application of two C14-labeled azo dyes. J. Toxicol and Environ Health. 18, 347-355, 1986.
15. Boeniger, M.: Carcinogenicity and metabolism of azo dyes, especially those derived from benzidine. DHHS(NIOSH) Publ. No. 80-119, 1980.
16. Lowry, L., Tolos, W., Boeniger, M., Nony, C., Bowman, M.: Chemical monitoring of urine from workers potentially exposed to benzidine-derived azo dyes. Toxicol Lett. 7, 29-36, 1980.
17. Bell, H., Breslin, P., and Lemen, K. Benzidine-, o-tolidine-, and o-dianisidine-based dyes. Health Hazard Alert. U.S. Department of Labor, OSHA and U.S. Department of Health and Human Services, PHS, CDC, NIOSH, DHEW(NIOSH) Publ. No. 81-106 1980.
18. NIOSH Recommendations for Occupational Safety and Health Standards. U.S. DHHS, PHS, CDC, NIOSH, Publ. No. (CDC) 85-8017.
19. Occupational Safety and Health Administration. Hazard Communication, Standards and Interpretations, 29 CFR 1910.1200, November 25, 1983.
20. National Toxicology Program, Fiscal year 1985 annual plan, DHHS, PHS, p. 138-141, 1985.
21. American Conference of Governmental Industrial Hygienists. Threshold limits values and biological exposure indices for 1985-86. ACGIH, Cincinnati, Ohio. ISBN: 0-936712-61-9.
22. Occupational Safety and Health Administration. OSHA standards 29 CFR 1910.1000. U.S. Dept. of Labor, OSHA 2206, revised June 1981.
23. Benzidine in urine (screening test) NIOSH Manual of Analytical Methods - Third Edition, Method 8304, Issued 2-15-84.
24. Benzidine in urine NIOSH Manual of Analytical Methods - Third Edition, Method 8306, Issued 2-15-84.

Table 1  
 Personal Air Exposure Monitoring Data for  
 O-dianisidine and O-dianisidine Dyes  
 Ciba-Geigy  
 Toms River Plant  
 Toms River, New Jersey  
 September 26, 1985  
 November 7, 15, 1986

Job Title	Sample No.	Time (min.)	o-Dianisidine ug/sample	Pure Dye ug/sample	Pure Dye, mg/m <sup>3</sup>	Total Dye, mg/m <sup>3</sup>
Chemical Operator	7	23	<0.6	--	ND	--
Chemical Operator	4	16	<0.6	--	ND	--
Venuleth Operator	9	32	22.0	83.2	0.87	1.64
Grinding Operator	24	128	9.7	36.7	0.10	0.19
Grinding Operator	25	156	<0.5	--	ND	--
Blending Operator	61	199	39.0	147.4	0.25	0.47
Blending Operator	62	40	4.4	16.6	0.14	0.26

o-d = O-dianisidine

ND = non-detectable

Limit of detection is <0.6 and <0.5 ug o-dianisidine per sample.

o-Dianisidine = the quantity of o-dianisidine recovered from the sample after reductive cleavage of the dye.

Pure Dye = the quantity of dye, minus any substances that are production by-products or additives.

Total Dye = Direct Black 91, the pure dye plus all other substances contained in the final product.

o-Dianisidine makes up 26.46% of pure C.I. Direct Black 91.

O-Dianisidine makes up approximately 14% of the total dye.

Pure C.I. Direct Black 91 makes up approximately 52.9% of the total dye.



Table 3  
 Area Air Monitoring Data for Total Dust  
 Ciba-Geigy  
 Toms River Plant  
 Toms River, New Jersey  
 September 26, 1985  
 November 7, 15, 1985

Location	Sample No.	Time (min.)	Total Dust mg/m <sup>3</sup>
Grinding and Blending area	FW6120	297	0.16
Grinding and Blending area	FW6116	338	0.17
Grinding and Blending area	FW6108	238	0.17

Limit of detection: 0.2 mg per sample

