

OSH INFORMATION MEMORANDUM 80-X-47

TO: All OSH Directors, Supervisors and Industrial Hygienists

FROM: William M. Lybrand, Director of OSH

SUBJECT: Benzidine-Based Dyes; Direct Black 38, Direct Brown 95 and Direct Blue 6 Dyes.

DATE: January 2, 1981

PURPOSE

This memorandum provides guidelines to follow when issuing citations under the General Duty Clause, Article I, Section 1.12, and pertinent standards of a general nature, for employee exposure to Direct Black 38, Direct Brown 75 and Direct Blue 6 Benzidine-based dyes.

BACKGROUND

Based on available scientific evidence, OSHA has determined that employee exposure to the three benzidine-based dyes covered in this memorandum presents a significant risk of cancer. Studies indicate that these dyes are carcinogenic in experimental animals. Additional studies indicate that these dyes are also metabolized in the body into benzidine, a human carcinogen. While OSHA has a specific standard to protect workers exposed to benzidine, these dyes cannot be covered under Article VI, Section 1910.1010. Although there are many other benzidine-based dyes, the toxicity data for them are not as complete as for the three dyes covered by this memorandum. However, the agency recommends that the other benzidine-based dyes also be handled as carcinogens.

a. Health Effects

1. In 1978 the National Cancer Institute (NCI) completed a 13-week sub chronic study of Direct Blue 6, Direct Black 38 and Direct Brown 95 using Fischer 344 rats. The results demonstrate that these dyes are both tumorigenic and carcinogenic, inducing both hepatic neoplastic nodules and hepatocellular carcinomas, respectively. (For reference source, see (g)(1) of this memorandum.)
2. An epidemiologic study by Yoshida, *et al.* (1971), demonstrated a probable association between bladder cancer and employee exposure to benzidine-based dyes. (For reference source, see (g)(2) of this memorandum.)

b. Biological Response.

1. Metabolism studies in five species of animals and in humans indicate that each of the three dyes is metabolized to benzidine, a known carcinogen. (See Appendix D of this memorandum.)
 2. A study of Direct Black 38 demonstrated that this dye is mutagenic in the Salmonella test system. (See Appendix D of this memorandum.)
- c. Source of the Dyes. In the United States, as of August 1979, Fabricolor Incorporated, Paterson, New Jersey, is the only known manufacturer of Direct Black 38, Direct Brown 95 and Direct Blue 6. However, importation of these three dyes supplements domestic production. The "Health Hazard Alert: Benzidine Derived Dyes" contains a list of importers. The distributors have not been identified by Federal OSHA.
- d. Synonyms, Physical Properties, and Structural Formulas. The synonyms, physical properties and structural formulas of these three dyes are detailed in this memorandum as follows:
1. Appendix A—Direct Black 38.
 2. Appendix B—Direct Brown 95.
 3. Appendix C—Direct Blue 6
- e. Manufacturing Process.
1. Fabricolor uses hydrazobenzene instead of benzidine as a starting material for manufacturing the dyes. The hydrazobenzene is dumped into a closed tank (reaction vessel) where it undergoes rearrangement to benzidine dihydrochloride by reaction with a strong solution of hydrochloric acid in water.

NOTE: The benzidine standard is applicable to this stage of the manufacturing process and remains applicable up to the state where the concentration of benzidine dihydrochloride drops below 0.1 percent by weight.
 2. The benzidine dihydrochloride solution is then reacted with sodium nitrate solution to form the diazo compound. This reaction could be carried out by adding the sodium nitrate solution to the benzidine hydrochloride solution, or alternatively by pumping the benzidine hydrochloride solution into another closed tank containing the sodium nitrate solution. Synthesis of the desired dye is continued by pumping the diazo compound to other reaction vessels for coupling to other compounds.
 3. After the final reaction is completed, the product is isolated from solution and moved to a filter press for filtering and the washing out of further impurities.
 4. The dye is taken from the filter press in press cake form and dried. Drying may be performed on a drum dryer after recreating a slurry of the dye; or drying may be done with a tray or a spray dryer.

5. The dried dye may be taken to a hammer mill and ground to a fine powder, or it may be taken directly to a ribbon blender. Color blending, standardization by adding salts and dedusting by adding dedusting oil is performed at the blender. The dye is transferred from the blender into drums for shipping.
- f. Uses. Some reported uses for the three dyes (for reference source, see 2. (g)(3) of this memorandum) are as follows:
1. Direct Black 38: Dyeing or staining of wool, silk, fibers for rope and matting, hogs hair, cotton and other cellulose, acetate, nylon and biological stains.
 2. Direct Brown 95: Dyeing or staining silk, cotton, acetate, cellulose, wool, nylon, leather, paper and certain plastics.
 3. Direct Blue 6: Dyeing or staining silk, wool, cotton, nylon, leather, paper, biological stains and writing inks.
- g. References.
1. Thirteen-week Subchronic Toxicity Studies of Direct Blue 6, Direct Black 38 and Direct Brown 95 Dyes. National Cancer Institute. Carcinogenesis Technical Report. DHEW Publication # "NIH" 78-1358, 1978.
 2. Yoshida, O., et al.: [Bladder cancer in workers of the dyeing industry.] Igaku No. Ayumi, Vol. 79, No. 7: 421-422, 1971. (Japanese)
 3. The Colour Index: 1971, 3rd Ed. Lund, Humphries, Bradford and London, eds. London, England: The Society of Dyers and Colourists- American Association of Textile Chemists and Colorists.
 4. Current Intelligence Bulletin 24: April 17, 1978. Benzidine Derived Dyes. National Institute for Occupational Safety and Health/National Cancer Institute

ENFORCEMENT

- a. Applicability of the General Duty Clause.
 1. Employee exposure to the three dyes covered in this memorandum has been established as a recognized hazard that is likely to cause death or serious physical harm. The recognition of the hazard has been established by two related facts:
 - (a) The National Cancer Institute (NCI), a preeminent authority on the testing of chemicals for carcinogenicity, has shown that the three dyes produce cancer in rats.

(b) This finding by the NCI has been widely published and disseminated to employers using the dyes. Some readily available sources which have reported the finding are as follows:

- (1) NCI's report. (See the full citation at (g)(1) of this memorandum.)
 - (2) Current Intelligence Bulletin #24, NCI/NIOSH. (See the full citation at (g)(4) of this memorandum.)
 - (3) American Industrial Hygiene Association Journal, Vol. 39, No. 8 August 1978, pp. A-18 to A-24. (Reprint of Current Intelligence Bulletin #24.)
 - (4) American Industrial Hygiene Association Journal, Vol. 39, No. 12, December 1978, p. A-20. (Reprint of "Industrial Alert" No. 3, issued by the Commonwealth of Virginia.)
 - (5) Jenkins, C.: Textile dyes are potential hazards, J. Environ. Health 40(5), 1978, pp. 279-284.
 - (6) "NCI says three dyes are animal carcinogens," Chemical & Engineering News, May 15, 1978, p. 12.
 - (7) "Hew institute Implicates Dyes In Cancer In Rats", Textile Chemist and Colorist, June 1978, pp. 7-8.
 - (8) "U.S. Links 3 Dyes to Rat Cancer," Daily News Record, New York, May 10, 1978.
2. The hazard to humans created by exposure to these three dyes is one that is likely to cause death or serious physical harm, since there is a significant association between bladder cancer and exposure to benzidine-based dyes. This conclusion is supported by Yoshida, et al., in their epidemiologic study. (See Appendix D of this memorandum.)
 3. Therefore, unless the employer could not, with the exercise of reasonable diligence, have known that any employees are exposed to one or more of the three dyes, the general duty clause (Article I, Section 1.12)

b. Case File Preparation.

- (1) Include the list of references presented in Appendix E in the case file. Also include references to any trade magazine articles that warn of the carcinogenicity of benzidine-based dyes.
- (2) Include as much as possible of the following documentation in the case file.

(a) Documentation of the awareness by the employer or the industry of any of the preceding communications.

(b) Documentation of the awareness by the employer or the industry of OSHA's standards for carcinogens.

c. Resource Allocations. Allocate resources in the following manner:

(1) Determine whether any of the three dyes covered by this memorandum is used when conducting either a health or safety inspection of an employer who:

- Dyes fabrics, paper, leather or plastics;
- Repackages dyes; or
- Produces writing ink or biological stains.

(2) When conducting either a health or safety inspection of an employer who cuts or sews textiles or leather, determine whether the material is dyed with any of the three dyes covered by this memorandum.

(3) Once an employer has been identified as a user of any of the three dyes, or has been found to cut or sew textiles or leather dyed with any of the three dyes, report the finding to the Assistant Director/OSH Compliance through the supervisory industrial hygienist. The Assistant Director/OSH Compliance shall determine whether and when to conduct an inspection involving the dyes. These inspections shall be conducted by or under the guidance of an industrial hygienist.

(4) Inspections shall take place when one or more of the three dyes is actually in use or when textiles or leather dyed with one of the dyes is actually being cut or sewn.

d. Determination of Whether the Dyes are used.

(1) Make these determinations by interviewing employers, employees and employee representatives, and by inspecting the labels on the employer's stocks of dyestuffs located in storerooms, laboratories and production areas. Check the names on the labels against the synonyms for the three dyes found in Appendixes A, B and C of this memorandum.

(2) If any of the dyes are used, determine the frequency of use and the quantity used.

(3) List other dyes that are encountered during a search for the three dyes. Place the list in the establishment file.

(4) Where other dyes are encountered include other benzidine-based dyes, ortho-tolidine-based dyes, and/or ortho-diansidine-based dyes, a copy of the hazard alert covering these dyes should have been given to and discussed with the employer.

- e. Determination of Whether Textiles or Leather that Are Cut or Sewn are Dyed with One of the Dyes Make these determinations by interviewing employers and by contacting the manufacturers who dyed the materials. Inspect labels and identification marks on bolts of material to aid in identifying the manufacturers who dyed the materials, as well as the product line or production run.
- f. Documentation that one or More of the Dyes is in Use. When conducting an inspection involving one or more of the dyes, documentation of the use must be made. Do this by photography whenever possible. This may include taking photographs showing employees transferring dye from the containers, supplemented by photographs of labels on the containers, photographs of formulation orders and/or photographs of production orders.
- g. Citations
 - (1) Issue citations for violation of Article I, Section 1.12 if employees are exposed to one or more of the three dyes by any route (inhalation, ingestion, skin absorption). With respect to exposure by inhalation, issue the citation regardless of whether respirators are used, provided it is feasible to prevent or reduce atmospheric contamination by engineering control measures or good work practices.
 - (2) Issue citations for violation of Article VI, Section 1910.134 (a)(1) if:
 - a. Employees are subjected to atmospheres contaminated with one or more of the three dyes, and
 - b. It is feasible to prevent or reduce the contamination by engineering control measures. (The 1910.134(a)(1) citation will require the implementation of engineering controls; and, to the extent that it duplicates part of the abatement procedures required by the Section 1.12 citation, the two citations should be cited in the alternative.)
 - (3) Issue citations for violation of appropriate Section 1910.134 provisions if employees exposed to atmospheres contaminated with one or more of the three dyes are not provided respiratory protection in accordance with these provisions.
 - (4) Issue citations for violation of Section 1910.132 and/or 1910.133 if employees who handle or are subject to accidental splashing or dusting with one or more of the dyes are not provided adequate protective clothing and/or equipment.
 - (5) Issue citations for violation of Section 1910.132 if employees who handle material that has not been washed after being dyed with one of the three dyes covered in this memorandum are not provided protective clothing that prevents skin contact with the dye on the material.
 - (6) Issue citations for violation of Article VI, Section 1910.141(d)(2) provisions if employees are not provided lavatories that accord with these provisions.

- (7) Issue citations for violation of Section 1910.141(d)(1) if lavatories and showers are not maintained in a sanitary condition.
 - (8) Issue citations for violation of Section 1910.141(g)(2) if employees eat or drink in an area exposed to one or more of the dyes.
- h. Documentation of Article VI, Section 1910.134(a)(1) Violations and Section 1.12 Violations for Exposing Employees.
- (1) Documentation of violations of section 1910.134(a)(1) will, in part, also serve to document violations of Section 1.12. This is because, in order to document violations of Section 1910.134(a)(1), it must be shown that:
 - (a) Employees work in harmful atmospheres contaminated with one or more of the three dyes, and
 - (b) It is feasible to reduce the contamination by engineering control measures.
 - (2) Section 1.12 may be used in addition to Section 1910.134(a)(1). The Section 1.12 citation would allege employee exposure to one or more of the dyes and list engineering controls, in addition to other applicable steps presented in this memorandum, as feasible methods of abating the hazard. Only those methods which OSHA can prove as being feasible should be listed in each case.
 - (3) Failure to document violations of Section 1910.134(a)(1) does not preclude the documentation of violations of Section 1.12. For example, inadequate respiratory protection, protective clothing, housekeeping, training, labeling, posting or contaminated areas, etc., can all cause exposure of employees, and thus can serve as a basis for issuance of Section 1.12 citations.
- i. Methods of Documenting Exposure.
- (1) The compliance officer must rely heavily on procedures other than sampling and chemical analysis to document exposure to the dyes. For example, compliance officers must take photographs that show poor work practices, lack of or improperly designed engineering controls, improperly maintained engineering controls, improperly maintained systems and equipment for processing or using the dyes, contaminated surfaces and/or soiled employees. Other documentary methods include taking measurements showing inadequate ventilation; interviewing employees, employee representatives, and employers; etc.
 - (2) However, in all cases samples shall be taken. Both bulk and air samples shall be taken when documenting exposure to the dyes by inhalation. When documenting exposure to the dyes by skin contact, bulk and wipe samples shall be taken and evidence demonstrating the contact shall be obtained; e.g., a photograph showing an employee's bare hand in contact with the dyes. When sampling:

- (a) The dyes should be sampled on glass fiber filters without organic binder at 2 liters per minute for a sampling time of 4 hours.
 - (b) Sample handling and shipment to the laboratory shall be that prescribed in the Industrial Hygiene Manual. Following receipt of the samples in the laboratory, they will be analyzed by high performance liquid chromatography for the specific dyes requested.
 - (c) Wipe samples of the dyes on normal working surfaces shall be collected on glass fiber filters without organic binders. For rough surfaces on which a glass fiber filter may tend to fall apart, a fluoropore filter may be used to collect the wipe sample.
 - (d) Collection and handling of the wipe samples shall be as prescribed in Chapter VI of the Industrial Hygienist Manual except for the type of filter used. These dyes are sensitive to light therefore, care should be taken not to expose the samples to high levels of indoor lighting or to direct sunlight.
 - (e) Regardless of whether air or wipe samples are to be analyzed, be sure to send bulk samples so that the labs can make up calibration curves.
- (3) These dyes have been shown to metabolize to benzidine, which may appear in the urine of exposed employees. Thus, some employers may be monitoring the benzidine in the urine of their employees who work with or around one or more of the dyes. With each employer, determine if this is the case. Where an employer does monitor the benzidine in employees' urine, and at least some results are positive, obtain copies of all results relevant to documenting exposure of employees to one or more of these dyes.
- j. When a determination is made to prepare a citation for exposing employees to one or more of the subject dyes, consider each of the conditions and practices listed in Appendix F of this memorandum that is determined to be applicable; check each conditional/practice on a copy of Appendix F and attach it to the citation with the notation on the citation that the items checked on Appendix F have been determined as feasible methods of abating the hazard described on the citation.

OSHA NATIONAL OFFICE REVIEW.

In the Federal letter transmitting OSHA Instruction 2-2.27 dated February 23, 1980, Subject: Same as this memorandum, to state designees, and in accordance with paragraph D.4.C. thereof, states were requested to cooperate with OSHA in all respects of the provisions of OSHA Instruction CPL 2-2.27. Paragraph G of that instruction provides for OSHA National Office Review of alleged violations as follows:

“G. National Office Review. Until instructed otherwise by the National Office, Area Offices conducting inspections where possible violations exist shall send copies of the entire case file dealing with violations and proposed citations to their Regional Offices, who will forward this material to the Office of Field Coordination and Experimental Programs prior to the issuance of any citations involving the three dyes covered in this memorandum. The Office of Field Coordination and Experimental Programs will then consult with the National Office of the Solicitor in determining whether citations should be issued.”

This Division shall implement this provision of OSHA Instruction CPL 2-2.27 as set forth in this paragraph 4.

EXPERT WITNESSES.

The OSHA National Office Directorate of Technical Support will assist in locating expert witness. In the event a citation for violation of the General Duty Clause is contested, the case presentation before the Hearing Officer should include expert witness testimony as to:

- a. The fact that there is sufficient evidence to demonstrate that the dye or dyes involved in the citation present a significant cancer risk to humans.
- b. The fact that the hazard is recognized in the industry, by the employer, or by a member of the health community who is associated with the employer, or the industry.
- c. The fact that methods of abatement presented in the citation are feasible.

EFFECTIVE DATE:

This memorandum is effective upon receipt and will remain in effect until cancelled or superseded.