

## PROGRAM DIRECTIVE

Program Directive A-96  
Issued September 1, 1981  
Revised May 8, 2000

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

**AFFECTED CODES/  
DIRECTIVES:** OAR 437-1910.1010, CPL 2-2.27

**PURPOSE:** This instruction provides guidelines to follow when issuing citations under ORS 654.010, and pertinent standards of a general nature, for employee exposure to Direct Black 38, Direct Brown 95, and Direct Blue 6 benzidine-based dyes.

**REFERENCES:** OSHA Instruction CPL 2-2.27

**BACKGROUND:** Based on federal OSHA program requirements and the lack of any specific standards dealing with benzidine-based dyes. This directive is to be followed once a compliance officer recognizes places of employment using the listed dyes.

Based on available scientific evidence, Federal OSHA has determined that employee exposure to the three benzidine - based dyes covered in this instruction 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 the Oregon Occupational Safety and Health Division (OR-OSHA) has a specific standard to protect workers exposed to benzidine, these dyes cannot be covered under OAR 437, Division 2/Z, Carcinogens (i.e., OAR 437-1910.1010, Benzidine). 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 directive. However, OR-OSHA 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 subchronic 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 (2)(g)(A) of this instruction.)
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 (2)(g)(B) of this instruction.)

B. Biological Response.

1. Metabolism studies in five species of animals and in humans indicated that each of the three dyes is metabolized to benzidine, a known carcinogen. (See Appendix D of this instruction.)
2. A study of Direct Black 38 demonstrated that this dye is mutagenic in the Salmonella test system. (See Appendix D of this instruction.)

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 or by OR-OSHA.

D. Synonyms, Physical Properties, and Structural Formulas. The synonyms, physical properties, and structural formulas of these three dyes are detailed in this instruction 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 stage where the concentration of benzidine dihydrochloride drops below 0.1 percent by weight.

2. The benzidine dihydrochloride solution is then reacted with sodium nitrite solution to form the diazo compound. This reaction could be carried out by adding the sodium nitrite solution to the benzidine hydrochloride solution, or alternatively by pumping the benzidine hydrochloride solution into another closed tank containing the sodium nitrite 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)(C) of this instruction) 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.

**ACTION:**

A. 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 design- ed 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 Field Operations 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, handling, and shipment of the wipe samples shall be as prescribed in Chapter VIII of the IHFOM except for the type of filter used. The dyes may be 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 the OH Laboratory 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.

B. Expert Witnesses.

OR-OSHA Technical Advisor with information and assistance from the Directorate of Technical Support through the Regional Offices will serve as an expert witness. In the event that an ORS 654.010 citation is contested, and an expert witness is necessary to testify before the review judge as to:

1. 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.
2. 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.
3. The fact that methods of abatement presented in the citation are feasible.

**EFFECTIVE**

**DATE:**

This directive is effective immediately and will remain in effect until cancelled or superseded.