

# Chlorazol Black

sc-214682



The Power to Question

## Material Safety Data Sheet

Hazard Alert Code  
Key:

EXTREME

HIGH

MODERATE

LOW

## Section 1 - CHEMICAL PRODUCT AND COMPANY IDENTIFICATION

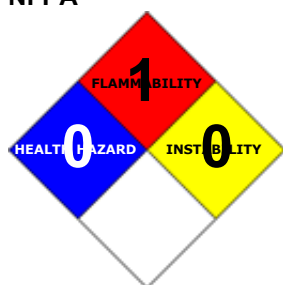
### PRODUCT NAME

Chlorazol Black

### STATEMENT OF HAZARDOUS NATURE

CONSIDERED A HAZARDOUS SUBSTANCE ACCORDING TO OSHA 29 CFR 1910.1200.

### NFPA



### SUPPLIER

Company: Santa Cruz Biotechnology, Inc.

Address:

2145 Delaware Ave

Santa Cruz, CA 95060

Telephone: 800.457.3801 or 831.457.3800

Emergency Tel: CHEMWATCH: From within the US and  
Canada: 877-715-9305

Emergency Tel: From outside the US and Canada: +800 2436  
2255 (1-800-CHEMCALL) or call +613 9573 3112

### PRODUCT USE

■ Direct dyes include water-soluble anionic azo dyes, which require the presence of electrolytes for the dyeing process. Most of the direct dyes are benzidine-based. They are classified as direct dyes, because they may be applied directly to celluloid fibres. Furthermore, they are used for colouring of rayon, paper, leather and to a less extent nylon. Dye for fabric, leather, cotton and cellulosics, vegetable-ivory buttons, wood flour used as a resin filler, typewriter ribbon, and to produce aqueous inks. May also have been used a component of hair dyes. Intermediate

### SYNONYMS

C34-H25-N9-O7-S2.2Na, "4-amino-3-[(4' -((2, 4-diaminophenyl)azo)(1, 1' -biphenyl)-4-yl)azo]-", "4-amino-3-[(4' -((2, 4-diaminophenyl)azo)(1, 1' -biphenyl)-4-yl)azo]-", "5-hydroxy-6-(phenylazo)-2, 7-naphthalenedisulfonic acid", "5-hydroxy-6-(phenylazo)-2, 7-naphthalenedisulfonic acid", "Airedale Black ED", "Direct Deep Black EH, GH, RH", "Atlantic Black BD, C, E, EA, ", "Atlantic Black GAC, GG, GXCW, GXOO, SD", "Benzo Deep Black E", "Benzo Leather Black E", "Brilliant Chrome Leather Black H", "Calcomine Black", "Chloramine Black C, EC, ERT, EX, EXR, XO", "Chlorazol Black E, Silk Black", "Direct Black", "Mitsui Direct Black EX, GX", "Paramine Black", "Phenamine Black", "Pontamine Black", "Sandopel Black", "Tetrazo Deep Black G", "Tetrodirect Black", "Union Black EM", "C.I. 30235", CI30235, "azo dye"

## Section 2 - HAZARDS IDENTIFICATION

### CANADIAN WHMIS SYMBOLS



### EMERGENCY OVERVIEW

#### RISK

May cause CANCER.

Possible risk of harm to the unborn child.

## POTENTIAL HEALTH EFFECTS

### ACUTE HEALTH EFFECTS

#### SWALLOWED

■ The material has NOT been classified as "harmful by ingestion". This is because of the lack of corroborating animal or human evidence. The material may still be damaging to the health of the individual, following ingestion, especially where pre-existing organ (e.g. liver, kidney) damage is evident. Present definitions of harmful or toxic substances are generally based on doses producing mortality (death) rather than those producing morbidity (disease, ill-health). Gastrointestinal tract discomfort may produce nausea and vomiting. In an occupational setting however, unintentional ingestion is not thought to be cause for concern.

#### EYE

■ There is some evidence that material may produce eye irritation in some persons and produce eye damage 24 hours or more after instillation. Moderate inflammation may be expected with redness; conjunctivitis may occur with prolonged exposure.

#### SKIN

■ The material is not thought to produce adverse health effects or skin irritation following contact (as classified using animal models). Nevertheless, good hygiene practice requires that exposure be kept to a minimum and that suitable gloves be used in an occupational setting.

■ Open cuts, abraded or irritated skin should not be exposed to this material.

■ Entry into the blood-stream, through, for example, cuts, abrasions or lesions, may produce systemic injury with harmful effects. Examine the skin prior to the use of the material and ensure that any external damage is suitably protected.

#### INHALED

■ The material is not thought to produce adverse health effects or irritation of the respiratory tract (as classified using animal models). Nevertheless, good hygiene practice requires that exposure be kept to a minimum and that suitable control measures be used in an occupational setting.

■ Persons with impaired respiratory function, airway diseases and conditions such as emphysema or chronic bronchitis, may incur further disability if excessive concentrations of particulate are inhaled.

■ Not normally a hazard due to non-volatile nature of product.

### CHRONIC HEALTH EFFECTS

■ There is sufficient evidence to suggest that this material directly causes cancer in humans.

Results in experiments suggest that this material may cause disorders in the development of the embryo or fetus, even when no signs of poisoning show in the mother.

Long term exposure to high dust concentrations may cause changes in lung function i.e. pneumoconiosis; caused by particles less than 0.5 micron penetrating and remaining in the lung. Prime symptom is breathlessness; lung shadows show on X-ray.

Azo dyes as a class are a concern for their potential induction of mutagenicity and carcinogenicity

Reductive cleavage or degradation into component aromatic amines is one of the mechanisms leading to the genotoxicity of azo dyes. The aromatic amines that arise from the azo reduction and cleavage of azo dyes are thought to be activated as mutagens through their N-oxidation by cytochrome P450 isozymes. The N-hydroxyarylamines that are formed may be further glucuronated (activated) or acetylated (inactivated), which may influence their mutagenicity. Under acidic pH, they form reactive nitrenium ions that can alkylate bases in DNA, particularly the nucleophilic centres in guanine. This mechanism is thought to contribute to the carcinogenicity of many azo dyes, and as a result, azo dyes should be assessed for toxicity and classified similarly to their component amines.

Many azo dyes (aromatic amines) have been found to be carcinogenic in laboratory animals, affecting the liver, urinary bladder and intestines. Specific toxicity effects in humans have not been established but some dyes are known to be mutagenic. Benzidine and its metabolic derivatives have been detected in the urine of workers exposed to Direct azo dyes. An epidemiological study of silk dyers and painters with multiple exposures to benzidine based and other dyes indicate a strong association with bladder cancer.

Not all azo dyes are genotoxic, only those dyes that contain either phenylenediamine or benzidine in the molecule would become mutagenic. Therefore, phenylenediamine and benzidine are the major mutagenic moieties of carcinogenic azo dyes. Many functional groups (i.e. NO<sub>2</sub>, CH<sub>3</sub> and NH<sub>2</sub>) within the molecules of these amines affected their genotoxicities. Many aromatic amines are carcinogenic and/or mutagenic. This appears to involve bioactivation by various organs and/ or bacterial intervention

The simplest azo dyes, which raise concern, have an exocyclic amino-group that is the key to any carcinogenicity for it is this group which undergoes biochemical N-oxidation and further reaction to reactive electrophiles. The DNA adducts formed by covalent binding through activated nitrogen have been identified. However not all azo compounds possess this activity and delicate alterations to structure vary the potential of carcinogenicity / acid, reduces or eliminates the effect. Complex azo dyes consisting of more than one azo (N=N) linkage may be metabolised to produce complexed carcinogenic aromatic amines such as benzidine.

The carcinogenic aromatic amines are generally recognized to be bioactivated in two steps: N-hydroxylation catalyzed by cytochrome P450 enzymes to give N-hydroxyarylamines and subsequent acetyl-CoA-dependent o-acetylation. The N-acetoxy esters formed by acetylation of hydroxylamines are reactive electrophiles which give rise to covalent DNA-adduct probably via the loss of an active anion, which yields a nitrenium ion.

In the past, azo colorants based on benzidine, 3,3'-dichlorobenzidine, 3,3'-dimethylbenzidine (o-tolidine), and 3,3'-dimethoxybenzidine (o-dianisidine) have been synthesized in large amounts and numbers. Studies in exposed workers have demonstrated that the azoreduction of benzidine-based dyes occurs in man. The metabolic conversion of benzidine-, 3,3'-dimethylbenzidine- and 3,3'-dimethoxybenzidine-based dyes to their (carcinogenic) amine precursors in vivo is a general phenomenon that must be considered for each member of this class of chemicals.

Azo dyes containing phenylenediamine are mutagenic in certain assays most likely due to the formation of oxidized p-phenylenediamine. p-Phenylenediamine are oxidised by the liver microsomal enzymes (S9). Pure p-phenylenediamine is non-mutagenic but becomes mutagenic after it is oxidized. Modification of the moieties that can be metabolized to p-phenylenediamine by sulfonation, carboxylation or copper complexation eliminated the mutagenic responses.

Bioavailability of azo dyes also determines whether they are to be metabolically converted to carcinogens. As a majority of azo pigments are based on 3,3'-dichlorobenzidine, much of the available experimental data are focused on this group. Long-term animal carcinogenicity studies performed with pigments based on 3,3'-dichlorobenzidine did not show a carcinogenic effect. Hence, it is very unlikely that occupational exposure to insoluble azo pigments would be associated with a substantial risk of (bladder) cancer in man. According to current EU regulations, azo dyes based on benzidine, 3,3'-dimethoxybenzidine and 3,3'-dimethylbenzidine have been classified as carcinogens of category 2 as "substances which should be regarded as if they are carcinogenic to man" This is not the case for 3,3'-dichlorobenzidine-based azo pigments.

It is also postulated that some of the aromatic amines metabolically produced from azo dyes may be responsible for the induction of autoimmune diseases such as lupus. This is probably due to the fact that lupus inducing drugs are amines in nature. They also have the similar metabolic activation pathways as the human bladder procarcinogens. The only difference between lupus inducing drugs and procarcinogens is that carcinogens interact with DNA to form covalent adducts which produce mutations, while lupus inducing drugs interact with DNA to provoke the immunoresponses.

Azo dyes are widely used in industry. A large amount of these dyes are discharged into streams and rivers, and they are

considered as an environmental pollutant. Some of these compounds may accumulate into food chains and eventually reach the human body through ingestion. Intestinal microbiota and to a lesser extent, the liver enzymes, are responsible for the cleavage of azo dyes into aromatic amines. Some of human endogenous bacteria that contaminate bladder can metabolically activate aromatic amines that are produced from azo dyes (procarcinogens). The addition of the nitro-group to these aromatic amines would convert them into direct mutagens.

These findings may also explain, partly, the close relationships between chronic infection and cancer development.

Skin bacteria are thought to be responsible for cleavage of certain azo dyes to produce carcinogens; of importance are dye-stuffs found in cosmetics, hair dyes, textiles and tattoo inks.

Several in vitro and in vivo studies suggest that certain azo dyes may be reductively cleaved when applied to the skin also under aerobic conditions. Results obtained with the various azo dyes suggest that reductive cleavage to aromatic amines has to be considered a significant degradation pathway. It is generally thought that about 30% of the dye may be cleaved in this manner.

From the available literature, on this chemical class of azo dyes, it can be deduced that all azo dyes which are split into carcinogenic arylamines are possible carcinogens.

Both water-soluble and lipophilic azo dyes of this class have been shown experimentally to undergo cleavage to potential carcinogens.

Several epidemiological studies of dye users suggest that there may be an excess mortality from bladder cancer in workers exposed to benzidine-based dyes. Inhalation or absorption through the skin has been recognised as a cause for these tumors. The carcinogenicity risk factor for workers exposed to benzidine is estimated to be 14 times higher than that of the unexposed population.

When administered in the diet, benzidine induced urinary bladder carcinomas in dogs and increased the incidence of benign and malignant cholangiomatous tumors and hepatocellular tumors in hamsters of both sexes. When administered by gavage benzidine induced multiple mammary carcinomas in female rats.

A survey of benzidine-exposed workers indicated that those with the lower than normal serum properdin levels were more likely to develop bladder tumours.

NIOSH recommends that three widely used benzidine-derived dyes, Direct Black 38, Direct Blue 6, and Direct Brown 95, be handled in the workplace as if they were human carcinogens. This recommendation is based primarily upon a preliminary analysis of National Cancer Institute (NCI) data from short-term feeding studies, and on early results from NIOSH field studies. Cancerous and precancerous liver conditions were found in rats, similar to the damage produced by known liver carcinogens. Degeneration of liver cells was found in mice. Although the dyes tested by NCI contained less than 4 ppm residual benzidine when fed to the test animals, greater quantities of benzidine were found in the urine of dosed rats and mice. Caution is also indicated by preliminary results from NIOSH field studies showing that humans working with these same dyes also excrete higher than expected levels of benzidine in their urine. Both laboratory and field studies indicate that these benzidine-derived dyes can be metabolized to benzidine which is present in the urine of animals and humans.

Based on the data from the short-term study, NCI scientists believe a cancer causing potential exists upon exposure to the benzidine-derived dyes, most likely through the mechanism of metabolic conversion of the dyes to benzidine in the animal system.

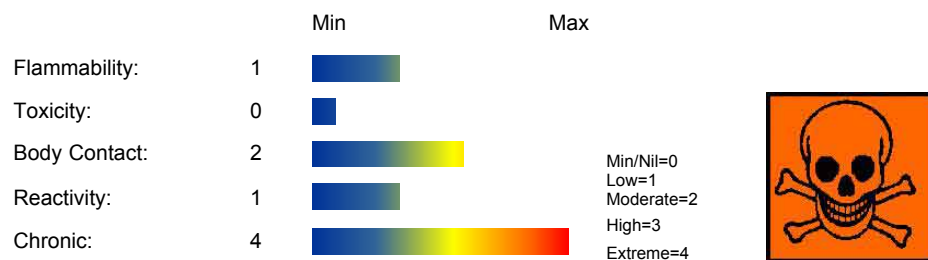
When administered in the diet Direct Black 38 induced hepatocellular carcinomas in male rats and neoplastic nodules of the liver in both sexes.

When administered in the drinking water Direct Black 38 induced papillomas and carcinomas of the liver, and adenocarcinomas of the colon of rats.

There was no evidence that the material was carcinogenic in mice when administered by these routes.

## Section 3 - COMPOSITION / INFORMATION ON INGREDIENTS

### HAZARD RATINGS



NAME	CAS RN	%
C.I. Direct Black 38	1937-37-7	100
commercial product may contain		
<a href="#">benzidine</a>	92-87-5	
<a href="#">4-aminodiphenyl</a>	92-67-1	
<a href="#">C.I. Solvent Orange 3, base</a>	495-54-5	

## Section 4 - FIRST AID MEASURES

### SWALLOWED

- 
- Immediately give a glass of water.
- First aid is not generally required. If in doubt, contact a Poisons Information Center or a doctor.

### EYE

- If this product comes in contact with the eyes:
  - Wash out immediately with fresh running water.
  - Ensure complete irrigation of the eye by keeping eyelids apart and away from eye and moving the eyelids by occasionally lifting the upper and lower lids.
  - If pain persists or recurs seek medical attention.
  - Removal of contact lenses after an eye injury should only be undertaken by skilled personnel.

## SKIN

- If skin or hair contact occurs:
  - Flush skin and hair with running water (and soap if available).
  - Seek medical attention in event of irritation.

## INHALED

- - If dust is inhaled, remove from contaminated area.
  - Encourage patient to blow nose to ensure clear passage of breathing.
  - If irritation or discomfort persists seek medical attention.

## NOTES TO PHYSICIAN

- Treat symptomatically.

Periodic medical surveillance should be carried out on persons in occupations exposed to the manufacture or bulk handling of the product and this should include hepatic function tests and urinalysis examination. [ILO Encyclopaedia].

## Section 5 - FIRE FIGHTING MEASURES

Vapour Pressure (mmHG):	Negligible
Upper Explosive Limit (%):	Not Available
Specific Gravity (water=1):	Not available
Lower Explosive Limit (%):	Not Available

## EXTINGUISHING MEDIA

- - Water spray or fog.
  - Foam.
  - Dry chemical powder.
  - BCF (where regulations permit).
  - Carbon dioxide.

## FIRE FIGHTING

- - Alert Emergency Responders and tell them location and nature of hazard.
  - Wear breathing apparatus plus protective gloves.
  - Prevent, by any means available, spillage from entering drains or water course.
  - Use water delivered as a fine spray to control fire and cool adjacent area.
  - DO NOT approach containers suspected to be hot.
  - Cool fire exposed containers with water spray from a protected location.
  - If safe to do so, remove containers from path of fire.
  - Equipment should be thoroughly decontaminated after use.

## GENERAL FIRE HAZARDS/HAZARDOUS COMBUSTIBLE PRODUCTS

- - Combustible solid which burns but propagates flame with difficulty.
  - Avoid generating dust, particularly clouds of dust in a confined or unventilated space as dusts may form an explosive mixture with air, and any source of ignition, i.e. flame or spark, will cause fire or explosion. Dust clouds generated by the fine grinding of the solid are a particular hazard; accumulations of fine dust may burn rapidly and fiercely if ignited.
  - Dry dust can be charged electrostatically by turbulence, pneumatic transport, pouring, in exhaust ducts and during transport.
  - Build-up of electrostatic charge may be prevented by bonding and grounding.
  - Powder handling equipment such as dust collectors, dryers and mills may require additional protection measures such as explosion venting.

Combustion products include: carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), nitrogen oxides (NO<sub>x</sub>), sulfur oxides (SO<sub>x</sub>), other pyrolysis products typical of burning organic material.

May emit corrosive fumes.

## FIRE INCOMPATIBILITY

- Avoid contamination with oxidizing agents i.e. nitrates, oxidizing acids, chlorine bleaches, pool chlorine etc. as ignition may result.

## PERSONAL PROTECTION

Glasses:

Safety Glasses.

Chemical goggles.

Gloves:

Respirator:

Particulate

## Section 6 - ACCIDENTAL RELEASE MEASURES

### MINOR SPILLS

- - Clean up waste regularly and abnormal spills immediately.
  - Avoid breathing dust and contact with skin and eyes.
  - Wear protective clothing, gloves, safety glasses and dust respirator.
  - Use dry clean up procedures and avoid generating dust.
  - Vacuum up or sweep up. NOTE: Vacuum cleaner must be fitted with an exhaust micro filter (HEPA type) (consider explosion-proof machines designed to be grounded during storage and use).
  - Dampen with water to prevent dusting before sweeping.

- Place in suitable containers for disposal.

#### MAJOR SPILLS

- 
- Clear area of personnel and move upwind.
- Alert Emergency Responders and tell them location and nature of hazard.
- Wear full body protective clothing with breathing apparatus.
- Prevent, by all means available, spillage from entering drains or water courses.
- Consider evacuation (or protect in place).
- No smoking, naked lights or ignition sources.
- Increase ventilation.
- Stop leak if safe to do so.
- Water spray or fog may be used to disperse / absorb vapour.
- Contain or absorb spill with sand, earth or vermiculite.
- Collect recoverable product into labelled containers for recycling.
- Collect solid residues and seal in labelled drums for disposal.
- Wash area and prevent runoff into drains.
- After clean up operations, decontaminate and launder all protective clothing and equipment before storing and re-using.
- If contamination of drains or waterways occurs, advise emergency services.

#### ACUTE EXPOSURE GUIDELINE LEVELS (AEGLE) (in ppm)

AEGLE 1: The airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience notable discomfort, irritation, or certain asymptomatic nonsensory effects. However, the effects are not disabling and are transient and reversible upon cessation of exposure.

AEGLE 2: The airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience irreversible or other serious, long-lasting adverse health effects or an impaired ability to escape.

AEGLE 3: The airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience life-threatening health effects or death.

## Section 7 - HANDLING AND STORAGE

### PROCEDURE FOR HANDLING

- 
- Avoid all personal contact, including inhalation.
- Wear protective clothing when risk of exposure occurs.
- Use in a well-ventilated area.
- Prevent concentration in hollows and sumps.
- DO NOT enter confined spaces until atmosphere has been checked.
- DO NOT allow material to contact humans, exposed food or food utensils.
- Avoid contact with incompatible materials.
- When handling, DO NOT eat, drink or smoke.
- Keep containers securely sealed when not in use.
- Avoid physical damage to containers.
- Always wash hands with soap and water after handling.
- Work clothes should be laundered separately.
- Launder contaminated clothing before re-use.
- Use good occupational work practice.
- Observe manufacturer's storing and handling recommendations.
- Atmosphere should be regularly checked against established exposure standards to ensure safe working conditions are maintained.

Empty containers may contain residual dust which has the potential to accumulate following settling. Such dusts may explode in the presence of an appropriate ignition source.

- Do NOT cut, drill, grind or weld such containers
- In addition ensure such activity is not performed near full, partially empty or empty containers without appropriate workplace safety authorisation or permit.

### RECOMMENDED STORAGE METHODS

- 
- Lined metal can, Lined metal pail/drum
- Plastic pail
- Polyliner drum
- Packing as recommended by manufacturer.
- Check all containers are clearly labeled and free from leaks.

Glass container.

### STORAGE REQUIREMENTS

- 
- Store in original containers.
- Keep containers securely sealed.
- Store in a cool, dry, well-ventilated area.
- Store away from incompatible materials and foodstuff containers.
- Protect containers against physical damage and check regularly for leaks.
- Observe manufacturer's storing and handling recommendations.

### SAFE STORAGE WITH OTHER CLASSIFIED CHEMICALS



X: Must not be stored together

O: May be stored together with specific preventions

+: May be stored together

## Section 8 - EXPOSURE CONTROLS / PERSONAL PROTECTION

### EXPOSURE CONTROLS

Source	Material	TWA ppm	TWA mg/m <sup>3</sup>	STEL ppm	STEL mg/m <sup>3</sup>	Peak ppm	Peak mg/m <sup>3</sup>	TWA F/CC	Notes
Canada - British Columbia Occupational Exposure Limits	benzidine (Benzidine)		(L)						Skin; A1, 1
Canada - Yukon Permissible Concentrations for Airborne Contaminant Substances	benzidine (K Benzidine production - Skin)		(See Table 15)						
Canada - British Columbia Occupational Exposure Limits	4-aminodiphenyl (4-Aminodiphenyl)		(L)						Skin; A1, 1
Canada - Yukon Permissible Concentrations for Airborne Contaminant Substances	4-aminodiphenyl (K 4-Aminodiphenyl - Skin)		(See Table 15)						
US OSHA Permissible Exposure Levels (PELs) - Table Z3	C.I. Solvent Orange 3, base (Inert or Nuisance Dust: (d) Respirable fraction)		5						
US OSHA Permissible Exposure Levels (PELs) - Table Z3	C.I. Solvent Orange 3, base (Inert or Nuisance Dust: (d) Total dust)		15						
US - Oregon Permissible Exposure Limits (Z3)	C.I. Solvent Orange 3, base (Inert or Nuisance Dust: (d) Respirable fraction)		5						*
US - Oregon Permissible Exposure Limits (Z3)	C.I. Solvent Orange 3, base (Inert or Nuisance Dust: (d) Total dust)		10						*

### MATERIAL DATA

C.I. DIRECT BLACK 38:

C.I. SOLVENT ORANGE 3, BASE:

■ Sensory irritants are chemicals that produce temporary and undesirable side-effects on the eyes, nose or throat. Historically occupational exposure standards for these irritants have been based on observation of workers' responses to various airborne concentrations. Present day expectations require that nearly every individual should be protected against even minor sensory irritation and exposure standards are established using uncertainty factors or safety factors of 5 to 10 or more. On occasion animal no-observable-effect-levels (NOEL) are used to determine these limits where human results are unavailable. An additional approach, typically used by the TLV committee (USA) in determining respiratory standards for this group of chemicals, has been to assign ceiling values (TLV C) to rapidly acting irritants and to assign short-term exposure limits (TLV STELs) when the weight of evidence from irritation, bioaccumulation and other endpoints combine to warrant such a limit. In contrast the MAK Commission (Germany) uses a five-category system based on intensive odour, local irritation, and elimination half-life. However this system is being replaced to be consistent with the European Union (EU) Scientific Committee for Occupational Exposure Limits (SCOEL); this is more closely allied to that of the USA.

OSHA (USA) concluded that exposure to sensory irritants can:

- cause inflammation
- cause increased susceptibility to other irritants and infectious agents
- lead to permanent injury or dysfunction
- permit greater absorption of hazardous substances and
- acclimate the worker to the irritant warning properties of these substances thus increasing the risk of overexposure.

C.I. DIRECT BLACK 38:

C.I. SOLVENT ORANGE 3, BASE:

■ It is the goal of the ACGIH (and other Agencies) to recommend TLVs (or their equivalent) for all substances for which there is evidence of health effects at airborne concentrations encountered in the workplace.

At this time no TLV has been established, even though this material may produce adverse health effects (as evidenced in animal experiments or clinical experience). Airborne concentrations must be maintained as low as is practically possible and occupational exposure must be kept to a minimum.

NOTE: The ACGIH occupational exposure standard for Particles Not Otherwise Specified (P.N.O.S) does NOT apply.

C.I. DIRECT BLACK 38:

■ WARNING: This substance is classified by the NOHSC as Category 2 Probable Human Carcinogen.

BENZIDINE:

■ For benzidines:

The high incidence of bladder tumours amongst workers exposed by inhalation and dermal routes has produced the recommendation that all exposures of benzidine be kept to an absolute minimum in the absence of an assigned TLV.

4-AMINODIPHENYL:

This compound is one of the most potent of the known bladder carcinogens. Workers exposed to the chemical should be properly equipped to eliminate to the fullest possible extent all exposures.



## PERSONAL PROTECTION



Consult your EHS staff for recommendations

### EYE

■

- Safety glasses with side shields.
- Chemical goggles.
- Contact lenses pose a special hazard; soft lenses may absorb irritants and all lenses concentrate them. DO NOT wear contact lenses.

### HANDS/FEET

■ Suitability and durability of glove type is dependent on usage. Important factors in the selection of gloves include: such as:

- frequency and duration of contact,
- chemical resistance of glove material,
- glove thickness and
- dexterity

Select gloves tested to a relevant standard (e.g. Europe EN 374, US F739).

- When prolonged or frequently repeated contact may occur, a glove with a protection class of 5 or higher (breakthrough time greater than 240 minutes according to EN 374) is recommended.
- When only brief contact is expected, a glove with a protection class of 3 or higher (breakthrough time greater than 60 minutes according to EN 374) is recommended.
- Contaminated gloves should be replaced.

Gloves must only be worn on clean hands. After using gloves, hands should be washed and dried thoroughly. Application of a non-perfumed moisturiser is recommended.

Experience indicates that the following polymers are suitable as glove materials for protection against undissolved, dry solids, where abrasive particles are not present.

- polychloroprene
- nitrile rubber
- butyl rubber
- fluorocautchouc
- polyvinyl chloride

Gloves should be examined for wear and/ or degradation constantly.

### OTHER

■

- Employees working with confirmed human carcinogens should be provided with, and be required to wear, clean, full body protective clothing (smocks, coveralls, or long-sleeved shirt and pants), shoe covers and gloves prior to entering the regulated area.
- Employees engaged in handling operations involving carcinogens should be provided with, and required to wear and use half-face filter-type respirators with filters for dusts, mists and fumes, or air purifying canisters or cartridges. A respirator affording higher levels of protection may be substituted.
- Emergency deluge showers and eyewash fountains, supplied with potable water, should be located near, within sight of, and on the same level with locations where direct exposure is likely.
- Prior to each exit from an area containing confirmed human carcinogens, employees should be required to remove and leave protective clothing and equipment at the point of exit and at the last exit of the day, to place used clothing and equipment in impervious containers at the point of exit for purposes of decontamination or disposal. The contents of such impervious containers must be identified with suitable labels. For maintenance and decontamination activities, authorized employees entering the area should be provided with and required to wear clean, impervious garments, including gloves, boots and continuous-air supplied hood.
- Prior to removing protective garments the employee should undergo decontamination and be required to shower upon removal of the garments and hood.
- Overalls.
- P.V.C. apron.
- Barrier cream.
- Skin cleansing cream.
- Eye wash unit.

■

- Respirators may be necessary when engineering and administrative controls do not adequately prevent exposures.
- The decision to use respiratory protection should be based on professional judgment that takes into account toxicity information, exposure measurement data, and frequency and likelihood of the worker's exposure - ensure users are not subject to high thermal loads which may result in heat stress or distress due to personal protective equipment (powered, positive flow, full face apparatus may be an option).
- Published occupational exposure limits, where they exist, will assist in determining the adequacy of the selected respiratory. These may be government mandated or vendor recommended.
- Certified respirators will be useful for protecting workers from inhalation of particulates when properly selected and fit tested as part of a complete respiratory protection program.
- Use approved positive flow mask if significant quantities of dust becomes airborne.
- Try to avoid creating dust conditions.

### RESPIRATOR

■

Protection Factor	Half-Face Respirator	Full-Face Respirator	Powered Air Respirator
10 x PEL	P1	-	PAPR-P1
	Air-line*	-	-

50 x PEL	Air-line**	P2	PAPR-P2
100 x PEL	-	P3	-
		Air-line*	-
100+ x PEL	-	Air-line**	PAPR-P3

\* - Negative pressure demand \*\* - Continuous flow

Explanation of Respirator Codes:

Class 1 low to medium absorption capacity filters.

Class 2 medium absorption capacity filters.

Class 3 high absorption capacity filters.

PAPR Powered Air Purifying Respirator (positive pressure) cartridge.

Type A for use against certain organic gases and vapors.

Type AX for use against low boiling point organic compounds (less than 65°C).

Type B for use against certain inorganic gases and other acid gases and vapors.

Type E for use against sulfur dioxide and other acid gases and vapors.

Type K for use against ammonia and organic ammonia derivatives

Class P1 intended for use against mechanically generated particulates of sizes most commonly encountered in industry, e.g. asbestos, silica.

Class P2 intended for use against both mechanically and thermally generated particulates, e.g. metal fume.

Class P3 intended for use against all particulates containing highly toxic materials, e.g. beryllium.

The local concentration of material, quantity and conditions of use determine the type of personal protective equipment required.

Use appropriate NIOSH-certified respirator based on informed professional judgement. In conditions where no reasonable estimate of exposure can be made, assume the exposure is in a concentration IDLH and use NIOSH-certified full face pressure demand SCBA with a minimum service life of 30 minutes, or a combination full facepiece pressure demand SAR with auxiliary self-contained air supply. Respirators provided only for escape from IDLH atmospheres shall be NIOSH-certified for escape from the atmosphere in which they will be used.

## ENGINEERING CONTROLS

- Employees exposed to confirmed human carcinogens should be authorized to do so by the employer, and work in a regulated area.
- Work should be undertaken in an isolated system such as a "glove-box" . Employees should wash their hands and arms upon completion of the assigned task and before engaging in other activities not associated with the isolated system.
- Within regulated areas, the carcinogen should be stored in sealed containers, or enclosed in a closed system, including piping systems, with any sample ports or openings closed while the carcinogens are contained within.
- Open-vessel systems are prohibited.
- Each operation should be provided with continuous local exhaust ventilation so that air movement is always from ordinary work areas to the operation.
- Exhaust air should not be discharged to regulated areas, non-regulated areas or the external environment unless decontaminated. Clean make-up air should be introduced in sufficient volume to maintain correct operation of the local exhaust system.
- For maintenance and decontamination activities, authorized employees entering the area should be provided with and required to wear clean, impervious garments, including gloves, boots and continuous-air supplied hood. Prior to removing protective garments the employee should undergo decontamination and be required to shower upon removal of the garments and hood.
- Except for outdoor systems, regulated areas should be maintained under negative pressure (with respect to non-regulated areas).
- Local exhaust ventilation requires make-up air be supplied in equal volumes to replaced air.
- Laboratory hoods must be designed and maintained so as to draw air inward at an average linear face velocity of 150 feet/ min. with a minimum of 125 feet/ min. Design and construction of the fume hood requires that insertion of any portion of the employees body, other than hands and arms, be disallowed.

## Section 9 - PHYSICAL AND CHEMICAL PROPERTIES

### PHYSICAL PROPERTIES

Solid.

Mixes with water.

State	Divided solid	Molecular Weight	781.78
Melting Range (°F)	Not available	Viscosity	Not Applicable
Boiling Range (°F)	Not available	Solubility in water (g/L)	Miscible
Flash Point (°F)	Not Available	pH (1% solution)	Not available
Decomposition Temp (°F)	Not available	pH (as supplied)	Not applicable
Autoignition Temp (°F)	Not available	Vapour Pressure (mmHG)	Negligible
Upper Explosive Limit (%)	Not Available	Specific Gravity (water=1)	Not available
Lower Explosive Limit (%)	Not Available	Relative Vapor Density (air=1)	Not applicable
Volatile Component (%vol)	Negligible	Evaporation Rate	Not applicable

### APPEARANCE

Black powder; mixes with water, ethanol, ethylene glycol monoethyl ether. The benzidine content of commercially produce Direct Black 38 ranges from 2-1254 mg/kg. The composition of commercial Direct Black 38 varies in order to meet individual shade and intensity requirements.

## Section 10 - CHEMICAL STABILITY

### CONDITIONS CONTRIBUTING TO INSTABILITY



- Product is considered stable and hazardous polymerization will not occur.

## STORAGE INCOMPATIBILITY

- Avoid reaction with oxidizing agents.

For incompatible materials - refer to Section 7 - Handling and Storage.

## Section 11 - TOXICOLOGICAL INFORMATION

C.I. Direct Black 38

### TOXICITY AND IRRITATION

- unless otherwise specified data extracted from RTECS - Register of Toxic Effects of Chemical Substances.

TOXICITY	IRRITATION
Oral (rat) LD50: 7600 mg/kg	Eye (rabbit): 100 mg - Moderate
■ The material may produce moderate eye irritation leading to inflammation. Repeated or prolonged exposure to irritants may produce conjunctivitis.	
• NOTE: Detailed analysis of the molecular structure, by various Authorities/ Agencies and in other cases by Chemwatch, indicates that the azo colourant can split off carcinogenic arylamines.	

The azo linkage is considered the most labile portion of an azo dye. The linkage easily undergoes enzymatic breakdown, but thermal or photochemical breakdown may also take place. The breakdown results in cleavage of the molecule and in release of the component amines. Water solubility determines the ultimate degradation pathways of the dyes. For example the azo linkage of many azo pigments is, due to very low solubility in water, not available for intracellular enzymatic breakdown but may be susceptible to endogenous micro-organisms found in the bladder or in the gut.

After cleavage of the azo linkage by bacteria, the component aromatic amines are absorbed in the intestine and excreted in the urine. Twenty-two of the component amines are recognised as potential human carcinogens, and/or several of them have shown carcinogenic potential on experimental animals. Sulfonation of the dye reduces the toxicity by enhancement of the excretion.

The component amines which may be released from azo dyes are mostly aromatic amines (compounds where an amine group or amine-generating group(s) are connected to an aryl moiety). In general, aromatic amines known as carcinogenic may be grouped into five groups

- Anilines, e.g. o-toluidine.
- Extended anilines, e.g. benzidine.
- Fused ring amines, e.g. 2-naphthylamine.
- Aminoazo and other azo compounds, e.g. 4-(phenylazo)aniline.
- Heterocyclic amines.

The aromatic amines containing moieties of anilines, extended anilines and fused ring amines are components of the majority of the industrially important azo dyes.

Reductive fission of the azo group, either by intestinal bacteria or by azo reductases of the liver and extra-hepatic tissues can cause benzidine-based aromatic amines to be released. Such breakdown products have been detected in animal experiments as well as in man (urine). Mutagenicity, which has been observed with numerous azo colourants in in vitro test systems, and the carcinogenicity in animal experiments are attributed to the release of amines and their subsequent metabolic activation. There are now epidemiological indications that occupational exposure to benzidine-based azo colourants can increase the incidence of bladder carcinoma.

The acute toxicity of azo dyes is low.. However, potential health effects are recognised.

Despite a very broad field of application and exposure, sensitising properties of azo dyes have been identified in relatively few reports. Red azoic dyes have been linked to allergic contact dermatitis in heavily exposed workers. Furthermore, textiles coloured with disperse azo dyes have caused allergic dermatitis in a few cases.

### The substance is classified by IARC as Group 3:

NOT classifiable as to its carcinogenicity to humans.

Evidence of carcinogenicity may be inadequate or limited in animal testing.

Tenth Annual Report on Carcinogens: Substance anticipated to be Carcinogen

[National Toxicology Program: U.S. Dep. of Health & Human Services 2002].

Substance has been investigated as tumorigenic by RTECs criteria in rat livers, other evidence equivocal.

### CARCINOGEN

DIRECT BLACK 38	US Environmental Defense Scorecard Recognized Carcinogens	Reference(s)	P65
DIRECT BLACK 38	US Environmental Defense Scorecard Suspected Carcinogens	Reference(s)	P65
Benzidine	International Agency for Research on Cancer (IARC) - Agents Reviewed by the IARC Monographs	Group	1
Benzidine	US EPA Carcinogens Listing	Carcinogenicity	A
Benzidine	US ACGIH Threshold Limit Values (TLV) - Carcinogens	Carcinogen Category	A
Benzidine	US ACGIH Threshold Limit Values (TLV) - Carcinogens	Carcinogen Category	A1
BENZIDINE	US Environmental Defense Scorecard Recognized Carcinogens	Reference(s)	P65
BENZIDINE	US Environmental Defense Scorecard Suspected Carcinogens	Reference(s)	P65
Benzidine	US Air Toxics Hot Spots TSD for Describing Available Cancer Potency Factors	IARC Class	1

Benzidine	US NIOSH Recommended Exposure Limits (RELs) - Carcinogens	Carcinogen	Ca
4-Aminobiphenyl	International Agency for Research on Cancer (IARC) - Agents Reviewed by the IARC Monographs	Group	1
4-Aminodiphenyl	US ACGIH Threshold Limit Values (TLV) - Carcinogens	Carcinogen Category	A1
4-AMINOBIIPHENYL	US Environmental Defense Scorecard Recognized Carcinogens	Reference(s)	P65
4-AMINOBIIPHENYL	US Environmental Defense Scorecard Suspected Carcinogens	Reference(s)	P65
4-Aminodiphenyl	US NIOSH Recommended Exposure Limits (RELs) - Carcinogens	Carcinogen	Ca

## SKIN

benzidine	Canada - Ontario Occupational Exposure Limits - Skin	Notes	Skin; Toxic Agent
benzidine	US AIHA Workplace Environmental Exposure Levels (WEELs) - Skin	Notes	Skin; Toxic Agent
benzidine	Canada - Quebec Permissible Exposure Values for Airborne Contaminants - Skin (French)	Notes	Skin; Toxic Agent
benzidine	US ACGIH Threshold Limit Values (TLV) - Skin	Skin Designation	Yes
benzidine	Canada - British Columbia Occupational Exposure Limits - Skin	Notation	Skin; A1, 1
benzidine	US - California Permissible Exposure Limits for Chemical Contaminants - Skin	Skin	S
4-aminodiphenyl	Canada - Ontario Occupational Exposure Limits - Skin	Notes	Skin; Toxic Agent
4-aminodiphenyl	US AIHA Workplace Environmental Exposure Levels (WEELs) - Skin	Notes	Skin; Toxic Agent
4-aminodiphenyl	Canada - Quebec Permissible Exposure Values for Airborne Contaminants - Skin (French)	Notes	Skin; Toxic Agent
4-aminodiphenyl	US ACGIH Threshold Limit Values (TLV) - Skin	Skin Designation	Yes
4-aminodiphenyl	Canada - British Columbia Occupational Exposure Limits - Skin	Notation	Skin; A1, 1
4-aminodiphenyl	US - California Permissible Exposure Limits for Chemical Contaminants - Skin	Skin	S

## Section 12 - ECOLOGICAL INFORMATION

Refer to data for ingredients, which follows:

C.I. SOLVENT ORANGE 3, BASE:

BENZIDINE:

■ Aromatic amines (arylamines), particularly primary aromatic amines, covalently and irreversibly bind to humic substances present in most natural waters.

All metabolites with moieties of: anilines, benzidines and toluidines are of environmental concern. Anilines and benzidines are both acutely toxic and toxic depending on the specific aquatic species (except algae). Toluidines represent a similar concern. It has been speculated that aqueous solutions of aromatic amines can be oxidised by organic radicals, but there are no actual data on reaction rates. Based on a study of reaction rate data for these compounds an estimate of the half-life of aromatic amines in water is approximately 100 days, assuming a peroxy radical concentration of 10<sup>-10</sup> mole/L in sunlit, oxygenated water.

■ Do NOT allow product to come in contact with surface waters or to intertidal areas below the mean high water mark. Do not contaminate water when cleaning equipment or disposing of equipment wash-waters.

Wastes resulting from use of the product must be disposed of on site or at approved waste sites.

■ Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment.

C.I. SOLVENT ORANGE 3, BASE:

C.I. DIRECT BLACK 38:

■ Biodegradation of azo dyes can occur in both aerobic and anaerobic environments. In both cases, the initial step in the biodegradation is the reductive cleavage of the azo-bond. Under aerobic conditions the initial step of cleavage of the azo-bond is typically followed by hydroxylation and ring opening of the aromatic intermediates.

The electron-withdrawal character of azo-groups generates electron deficiency and thus makes the compounds less susceptible to oxidative catabolism. As a consequence, many of these chemicals tend to persist under aerobic environmental conditions. Aerobic degradation of azo dyes is not expected as oxygen is often an inhibitor of azo reduction. Biodegradation of these dyes by aerobic sludge is reported to be insignificant as greater than 50% of the dye remains unchanged or is only slightly modified.

Reduction of azo dyes occurs primarily under anaerobic conditions through cleavage of the azo linkage. While azo dyes are generally stable under aerobic conditions, they are susceptible to reductive degradation under the anaerobic conditions characteristic of sediment. A possible pathway of azo dye degradation is azo-reductase under anaerobic conditions followed by mineralisation under aerobic conditions, with the resultant end products being NH<sub>3</sub>, CO<sub>2</sub> and H<sub>2</sub>O.

The great majority of azo dyes are water soluble and they colour different substrates by becoming physically attached. The attachment may be due to adsorption, absorption or mechanical adherence. Most of the commercial available azo dyes are in fact formulations of several components in order to improve the technical properties of the dyeing process.

The content of a specific dye lies in the range of 10 to 98%.

Soluble azo dyes, which are likely to remain in solution and therefore are unlikely to adsorb to sediment or sludge, the above anaerobic pathway is unlikely to occur.

An important natural abiotic degradation mechanism is photolysis and hydrolysis as a function of pH in the range of pH 4-9. The evidence of the role of hydrolysis in degradation of azo dyes is not conclusive. Even though the dyes have absorption maxima in the range of visible and UV-light, photo-reduction does not play a dominant role in the environmental fate of dyes,

although its contribution to the total mineralisation of widely dispersed trace amounts may be underestimated. Furthermore, hydrolysis seems not to be an important degradation pathway either, except for reactive dyes, which are hydrolysed rapidly in aqueous solution. For the metabolites, photolysis may be of some importance, whereas hydrolysis does not seem to be an important degradation route.

If the dye is not broken during rigors of biological waste treatment, it is unlikely to degrade rapidly in the less severe conditions of the environment. The reductive cleavage of the azo-bond is the major degradation pathway for azo dyes. Photo-reduction of azo dyes to hydrazines and amines is possible, but it is likely to be very slow, except in oxygen-poor water. The stability of the dyes to visible and UV-light is very high, and therefore only slow degradation has been shown. The photo-stability of azo dyestuffs is high in pure water but in the presence of natural humic materials, the photo decomposition is strongly accelerated, probably through oxidation by single oxygen or oxy-radicals

Although azo dyes are generally not readily or inherently biodegradable, bioaccumulation or adsorption to sediment is not expected due to their, generally, low partition coefficient

Certain of the Acid and Basic azo dyes are acutely toxic to aquatic organisms (fish, crustaceans, algae and bacteria); this is also true of some Direct dyes. Reactive dyes generally have very high effect concentration levels (>100 mg/l) and are not considered to be toxic to aquatic organisms. The non-ionic (Disperse and Solvent) dyes are toxic or potentially toxic. Solvent dyes may even be acutely toxic to aquatic organisms. The Mordant dyes (nonionics) generally do not exhibit any toxicity at levels below 100 mg/l.

4-AMINODIPHENYL:

C.I. SOLVENT ORANGE 3, BASE:

BENZIDINE:

■ DO NOT discharge into sewer or waterways.

C.I. DIRECT BLACK 38:

■ for ionic dyes:

Environmental fate:

In general the ionic dyes will be almost completely or partly dissociated in an aqueous solution. Solubility in the range 100 mg/l to 80,000 mg/l has been reported for the ionic azo dyes. In addition, they would be expected to have a high to a moderate mobility in soil, sediment and particular matter, indicated by the low Koc values. However, due to their ionic nature, they adsorb as a result of ion-exchange processes.

Based on the properties of sediments, anion exchange is anticipated to be extensive and rapid for the for the anionic acid and direct dyes. A high degree of adsorption occurs with direct apparently unrelated to the number of sulfonic acid groups (in contrast to the more soluble acid dyes).

In addition, ionic compounds are not considered to be able to volatilise neither from moist nor dry surfaces, and the vapour pressures for these dyes are very low.

Direct dyes (Direct Red 28, Direct Blue 1 and Direct Blue 14) are degraded with more than 90% in anaerobic sediment-water systems with half-lives ranging from 2 to 16 days. The degradation is inhibited when the dyes are strongly bound to the sediment.

With few exceptions, it appears that the very hydrophilic (ionic) dyes have a log BCF of - 1 to 1, although from the log Kow lower experimental log BCFs may have been predicted than have been actually measured. This is explained by the adherence of dyes to the outside of the fish or to the intestine. None of the dyestuffs bearing at least one charged group has showed a log BCF larger than 1.

Many dyes are visible in water at concentrations as low as 1 mg/l. Textile-processing waste waters, typically with a dye content in the range 10- 200 mg /l are therefore usually highly coloured and discharge in open waters presents an aesthetic problem. As dyes are designed to be chemically and photolytically stable, they are highly persistent in natural environments. It is thus unlikely that they, in general, will give positive results in short-term tests for aerobic biodegradability. The release of dyes may therefore present an ecotoxic hazard and introduces the potential danger of bioaccumulation that may eventually affect man by transport through the food chain

Ecotoxicity:

Algae are generally susceptible to dyes, but the inhibitory effect is thought to be related to light inhibition at high dye concentrations, rather than a direct inhibitory effect of the dyes. This effect may account for up to 50% of the inhibition observed.

Virtually all dyes from all chemically distinct groups are prone to fungal oxidation but there are large differences between fungal species with respect to their catalysing power and dye selectivity. A clear relationship between dye structure and fungal dye biodegradability has not been established. Fungal degradation of aromatic structures is a secondary metabolic event that starts when nutrients (C, N and S) become limiting. Therefore, while the enzymes are optimally expressed under starving conditions, supplementation of energy substrates and nutrients are necessary for propagation of the cultures.

The effects of the substitutional pattern of the dyes are inconclusive, but it has been suggested that introduction of the functional groups; methyl, nitro, sulfo or acid, weakens the inhibition of bacteria, whereas introduction of chlorine and bromine strengthens the inhibition.

BENZIDINE:

■ Hazardous Air Pollutant:	Yes
■ Fish LC50 (96hr.) (mg/l):	20
■ log Kow (Prager 1995):	1.34
■ log Kow (Sangster 1997):	1.34
■ Half- life Soil - High (hours):	192
■ Half- life Soil - Low (hours):	48
■ Half- life Air - High (hours):	3.12
■ Half- life Air - Low (hours):	0.312
■ Half- life Surface water - High (hours):	192
■ Half- life Surface water - Low (hours):	31.2
■ Half- life Ground water - High (hours):	384
■ Half- life Ground water - Low (hours):	96
■ Aqueous biodegradation - Aerobic - High (hours):	192
■ Aqueous biodegradation - Aerobic - Low (hours):	48
■ Aqueous biodegradation - Anaerobic - High (hours):	768
■ Aqueous biodegradation - Anaerobic - Low (hours):	192
■ Aqueous biodegradation - Removal secondary treatment - High (hours):	91%
■ Aqueous biodegradation - Removal secondary treatment - Low (hours):	65%

■ Photooxidation half- life water - High (hours):	1740
■ Photooxidation half- life water - Low (hours):	31.2
■ Photooxidation half- life air - High (hours):	3.12
■ Photooxidation half- life air - Low (hours):	0.312

#### ■ For benzidine:

##### Environmental Fate

**Terrestrial Fate:** Koc values in the range of 227,000 to 882,000, measured in 4 soils, indicate that benzidine is expected to be essentially immobile in soil. Benzidine is a weak base with 2 amine functional groups having pKa values of 4.3 and 3.3. These values indicate that benzidine can partially exist in the protonated form under acidic conditions. Volatilisation of the neutral species of benzidine from moist soil surfaces is not expected to be an important fate process given an estimated Henry's Law constant of  $5.2 \times 10^{-11}$  atm-cu m/mole. The conjugate acid will not volatilise since cations are non-volatile. Benzidine is not expected to volatilise from dry soil surfaces based upon an estimated vapor pressure of  $7 \times 10^{-7}$  mm Hg, determined from a fragment constant method. Benzidine is generally resistant to biodegradation in soil at high concentrations, but may biodegrade at lower concentrations. Aqueous solutions of benzidine (0.01%) were reported to be stable for 9 weeks to degradation by soil/river water inoculum. In Drummer silty clay loam, benzidine applied at a concentration of 10 ppb was degraded 79% after 4 weeks. Benzidine is rapidly oxidized by Fe(III) and other cations which are frequently found in soils and clay.

**Aquatic fate:** Koc values of benzidine indicate that benzidine is expected to adsorb to suspended solids and sediment. Volatilisation of the free base from water surfaces is not expected based upon an estimated Henry's Law constant. The conjugate acid will not volatilise. BCF values of 40 and 55 measured in fish, suggest bioconcentration in aquatic organisms is moderate. When aerated solutions of benzidine (100 ppb) were exposed to light from a xenon lamp (300-400 nm), complete degradation was observed in 12 hrs. Aqueous solutions of benzidine (0.01%) were reported to be stable for 9 weeks to degradation by soil/river water inoculum.

**Atmospheric fate:** According to a model of gas/particle partitioning of semivolatile organic compounds in the atmosphere and vapour pressure, benzidine, is expected to exist in both the vapour and particulate phases in the ambient atmosphere. Vapor-phase benzidine is degraded in the atmosphere by reaction with photochemically-produced hydroxyl radicals; the half-life for this reaction in air is estimated to be 2 hours, calculated from its rate constant of  $1.5 \times 10^{-10}$  cu cm/molecule-sec at 25 deg C. Benzidine also absorbs light greater than 290 nm and may undergo direct photolysis. Over 40% photodegradation was observed when benzidine adsorbed to silica gel plates was irradiated with UV light > 290 nm for 17 hours. Particulate- phase benzidine may be removed from the air by wet and dry deposition.

##### Ecotoxicity:

Fish LC50 (96 h): scud (*Gammarus pseudolimnaeus*) >20 mg/l; fathead minnow (*Pimephales promelus*) >20 mg/l; rainbow trout (*Salmo gairdneri*) 7.4 mg/l (static bioassay); *Salvelinus namaycush* 4.35 mg/l (static bioassay); *Notropis lutrensis* 2.5 mg/l (static bioassay); flagfish (*Jordanella floridae*) 16.2 mg/l (static bioassay).

##### 4-AMINODIPHENYL:

■ Hazardous Air Pollutant:	Yes
■ Half- life Soil - High (hours):	168
■ Half- life Soil - Low (hours):	24
■ Half- life Air - High (hours):	6
■ Half- life Air - Low (hours):	0.6
■ Half- life Surface water - High (hours):	168
■ Half- life Surface water - Low (hours):	24
■ Half- life Ground water - High (hours):	336
■ Half- life Ground water - Low (hours):	48
■ Aqueous biodegradation - Aerobic - High (hours):	168
■ Aqueous biodegradation - Aerobic - Low (hours):	24
■ Aqueous biodegradation - Anaerobic - High (hours):	672
■ Aqueous biodegradation - Anaerobic - Low (hours):	96
■ Photooxidation half- life water - High (hours):	3480
■ Photooxidation half- life water - Low (hours):	62.4
■ Photooxidation half- life air - High (hours):	6
■ Photooxidation half- life air - Low (hours):	0.6

■ PAHs travel through the atmosphere as a gas or attached to dust particles. They are carried by air currents and deposited by dry or wet (rain, dew, etc) deposition. When deposited in water they sink to the bottom of lakes and rivers. Some will move through the soil to contaminate groundwater.

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous in the marine environment, occurring at their highest environmental concentrations around urban centres.

Two factors, lipid and organic carbon, control to a large extent the partitioning behaviour of PAHs in sediment, water and tissue; the more hydrophobic a compound, the greater the partitioning to non-aqueous phases. These two factors, along with the octanol-water partition coefficient, are the best predictors of this partitioning and can be used to determine PAH behaviour and its bioavailability in the environment.

The lipid (fat) phase, of all organisms, contains the highest levels of PAHs: organic carbon associated with sediment or dissolved in water has a great influence on bioavailability resulting from its ability to adsorb.

Accumulation of PAHs occurs in all marine organisms; however there is a wide range in tissue concentrations resulting from variable environmental concentrations, level and time of exposure, and species ability to metabolize these compounds. PAHs generally partition in lipid-rich tissues and their metabolites are found in most tissues. In fish, bile and liver accumulate the highest levels of parent PAH and metabolites. In invertebrates, the highest concentrations can be found in the internal organs, such as the liver and pancreas; tissue concentrations appear to follow seasonal cycles which may be related to variations in lipid content or spawning cycles.

The primary mode of toxicity for PAHs in soil dwelling terrestrial invertebrates is non-specific non-polar narcosis. The uptake of PAHs by earthworms occurs primarily by direct contact with the soluble phase of soil solution (interstitial pore-water).

Microbial degradation of PAHs is a key process in soils. Biodegradation of PAHs may take place over a period of weeks to months. Mixed microbial populations in sediment/water systems may degrade some PAHs, with degradation progressively decreasing with increasing molecular weight. The rate of degradation is dependent on nutrient content and the bacterial community in soil.

PAHs in soils undergo a weathering process such that the lighter chain fractions are removed (primarily by volatilisation). Heavier fractions bind to soil organic matter and remain behind in the top soil horizon. As the mixture of PAHs age, bioavailability changes as the fraction remaining bind more tightly.

In general the more soluble a PAH, the higher the uptake by plants while the reverse is true for uptake by earthworms and uptake in the gastrointestinal tract of animals.

C.I. SOLVENT ORANGE 3, BASE:

#### Ecotoxicity

Ingredient	Persistence: Water/Soil	Persistence: Air	Bioaccumulation	Mobility
C.I. Direct Black 38	HIGH		LOW	LOW
benzidine	LOW	LOW	LOW	MED
4-aminodiphenyl	LOW	LOW	LOW	MED
C.I. Solvent Orange 3, base	HIGH		LOW	MED

## Section 13 - DISPOSAL CONSIDERATIONS

### US EPA Waste Number & Descriptions

#### B. Component Waste Numbers

When benzidine is present as a solid waste as a discarded commercial chemical product, off-specification species, as a container residue, or a spill residue, use EPA waste number U021 (waste code T).

#### Disposal Instructions

All waste must be handled in accordance with local, state and federal regulations.

! Puncture containers to prevent re-use and bury at an authorized landfill.

Legislation addressing waste disposal requirements may differ by country, state and/ or territory. Each user must refer to laws operating in their area. In some areas, certain wastes must be tracked.

A Hierarchy of Controls seems to be common - the user should investigate:

- Reduction
- Reuse
- Recycling
- Disposal (if all else fails)

This material may be recycled if unused, or if it has not been contaminated so as to make it unsuitable for its intended use. Shelf life considerations should also be applied in making decisions of this type. Note that properties of a material may change in use, and recycling or reuse may not always be appropriate.

DO NOT allow wash water from cleaning equipment to enter drains. Collect all wash water for treatment before disposal.

- Recycle wherever possible.
- Consult manufacturer for recycling options or consult Waste Management Authority for disposal if no suitable treatment or disposal facility can be identified.
- Dispose of by: Burial in a licensed land-fill or Incineration in a licensed apparatus (after admixture with suitable combustible material)
- Decontaminate empty containers. Observe all label safeguards until containers are cleaned and destroyed.

## Section 14 - TRANSPORTATION INFORMATION

NOT REGULATED FOR TRANSPORT OF DANGEROUS GOODS: DOT, IATA, IMDG

## Section 15 - REGULATORY INFORMATION

### C.I. Direct Black 38 (CAS: 1937-37-7) is found on the following regulatory lists;

"Canada Domestic Substances List (DSL)", "Canada Ingredient Disclosure List (SOR/88-64)", "Canada Toxicological Index Service - Workplace Hazardous Materials Information System - WHMIS (English)", "Canada Toxicological Index Service - Workplace Hazardous Materials Information System - WHMIS (French)", "International Chemical Secretariat (ChemSec) REACH SIN\* List (\*Substitute It Now!) 1.0", "US - California Air Toxics ""Hot Spots"" List (Assembly Bill 2588) Substances for which emissions must be quantified", "US - California Occupational Safety and Health Regulations (CAL/OSHA) - Hazardous Substances List", "US - California Proposition 65 - Carcinogens", "US - California Proposition 65 - No Significant Risk Levels (NSRLs) for Carcinogens", "US - Connecticut Hazardous Air Pollutants", "US - Maine Chemicals of High Concern List", "US - Minnesota Hazardous Substance List", "US - Pennsylvania - Hazardous Substance List", "US - Rhode Island Hazardous Substance List", "US DOE Temporary Emergency Exposure Limits (TEELs)", "US EPCRA Section 313 Chemical List", "US List of Lists - Consolidated List of Chemicals Subject to the Emergency Planning and Community Right-to-Know Act (EPCRA) and Section 112(r) of the Clean Air Act", "US Toxic Substances Control Act (TSCA) - Inventory", "US TSCA Section 12(b) - List of Chemical Substances Subject to Export Notification Requirements", "US TSCA Section 5(a)(2) - Significant New Use Rules (SNURs)", "US TSCA Section 8 (d) - Health and Safety Data Reporting"

Regulations for ingredients

### benzidine (CAS: 92-87-5) is found on the following regulatory lists;

"Canada - British Columbia Occupational Exposure Limits", "Canada - Nova Scotia Occupational Exposure Limits", "Canada - Ontario Occupational Exposure Limits", "Canada - Prince Edward Island Occupational Exposure Limits", "Canada - Quebec Permissible Exposure Values for Airborne Contaminants (English)", "Canada - Saskatchewan Environmental Persistent or Chronic Hazardous Substances", "Canada - Saskatchewan Occupational Health and Safety Regulations - Notifiable Chemical Substances", "Canada - Yukon Permissible Concentrations for Airborne Contaminant Substances", "Canada ARET (Accelerated Reduction / Elimination of Toxics) Substance List", "Canada Ingredient Disclosure List (SOR/88-64)", "Canada Non-Domestic Substances List (NDSL)", "Canada Priority Substances List (PSL1, PSL 2)", "Canada Prohibited Toxic Substances - Schedule 2: Permitted Uses (English)", "Canada Prohibited Toxic Substances - Schedule 2: Reporting Thresholds (English)", "Canada Toxicological Index Service - Workplace Hazardous Materials Information System - WHMIS (English)", "Canada Toxicological Index Service - Workplace Hazardous Materials Information System - WHMIS (French)", "International Agency for Research on Cancer (IARC) - Agents Reviewed by the IARC Monographs", "International Chemical Secretariat (ChemSec) REACH SIN\* List (\*Substitute It Now!) 1.0", "US - Alaska Limits for Air Contaminants", "US - California Air Toxics ""Hot Spots"" List (Assembly Bill 2588) Substances for which emissions must be quantified", "US - California Occupational Safety and Health Regulations (CAL/OSHA) - Hazardous Substances List", "US - California Permissible Exposure Limits for Chemical Contaminants", "US - California Proposition 65 - No Significant Risk Levels (NSRLs) for Carcinogens", "US - California Proposition 65 - Priority List



for the Development of NSRLs for Carcinogens", "US - California Toxic Air Contaminant List Category V", "US - Connecticut Hazardous Air Pollutants", "US - Hawaii Air Contaminant Limits", "US - Idaho - Limits for Air Contaminants", "US - Massachusetts Oil & Hazardous Material List", "US - Michigan Exposure Limits for Air Contaminants", "US - Minnesota Hazardous Substance List", "US - Minnesota Permissible Exposure Limits (PELs)", "US - New Jersey Right to Know Hazardous Substances", "US - Oregon Permissible Exposure Limits (Z1)", "US - Pennsylvania - Hazardous Substance List", "US - Rhode Island Hazardous Substance List", "US - Tennessee Occupational Exposure Limits - Limits For Air Contaminants", "US - Vermont Hazardous Constituents", "US - Vermont Hazardous wastes which are Discarded Commercial Chemical Products or Off-Specification Batches of Commercial Chemical Products or Spill Residues of Either", "US - Vermont Permissible Exposure Limits Table Z-1-A Final Rule Limits for Air Contaminants", "US - Vermont Permissible Exposure Limits Table Z-1-A Transitional Limits for Air Contaminants", "US - Washington Dangerous waste constituents list", "US - Washington Discarded Chemical Products List - ""U"" Chemical Products", "US - Washington General Occupational Health Standards - List of Carcinogens", "US - Wyoming Toxic and Hazardous Substances Table Z1 Limits for Air Contaminants", "US ACGIH Threshold Limit Values (TLV)", "US ACGIH Threshold Limit Values (TLV) - Carcinogens", "US CERCLA Priority List of Hazardous Substances", "US Clean Air Act - Hazardous Air Pollutants", "US CWA (Clean Water Act) - Priority Pollutants", "US CWA (Clean Water Act) - Toxic Pollutants", "US Department of Transportation (DOT) List of Hazardous Substances and Reportable Quantities - Hazardous Substances Other Than Radionuclides", "US DOE Temporary Emergency Exposure Limits (TEELs)", "US EPA Carcinogens Listing", "US EPA National Priorities List - Superfund Chemical Data Matrix (SCDM) - Hazard Ranking System - Hazardous Substance Benchmarks", "US EPCRA Section 313 Chemical List", "US List of Lists - Consolidated List of Chemicals Subject to the Emergency Planning and Community Right-to-Know Act (EPCRA) and Section 112(r) of the Clean Air Act", "US National Toxicology Program (NTP) 11th Report Part A Known to be Human Carcinogens", "US NFPA 30B Manufacture and Storage of Aerosol Products - Chemical Heat of Combustion", "US NIOSH Recommended Exposure Limits (RELs)", "US OSHA Carcinogens Listing", "US OSHA Permissible Exposure Levels (PELs) - Table Z1", "US RCRA (Resource Conservation & Recovery Act) - Hazardous Constituents - Appendix VIII to 40 CFR 261", "US RCRA (Resource Conservation & Recovery Act) - List of Hazardous Wastes", "US Toxic Substances Control Act (TSCA) - Inventory", "US TSCA Section 12(b) - List of Chemical Substances Subject to Export Notification Requirements", "US TSCA Section 5(a)(2) - Significant New Use Rules (SNURs)", "US TSCA Section 8 (d) - Health and Safety Data Reporting"

**4-aminodiphenyl (CAS: 92-67-1) is found on the following regulatory lists;**

"Canada - British Columbia Occupational Exposure Limits", "Canada - Nova Scotia Occupational Exposure Limits", "Canada - Ontario Occupational Exposure Limits", "Canada - Prince Edward Island Occupational Exposure Limits", "Canada - Quebec Permissible Exposure Values for Airborne Contaminants (English)", "Canada - Saskatchewan Environmental Persistent or Chronic Hazardous Substances", "Canada - Saskatchewan Occupational Health and Safety Regulations - Notifiable Chemical Substances", "Canada - Yukon Permissible Concentrations for Airborne Contaminant Substances", "Canada ARET (Accelerated Reduction / Elimination of Toxics) Substance List", "Canada Ingredient Disclosure List (SOR/88-64)", "Canada Non-Domestic Substances List (NDSL)", "International Agency for Research on Cancer (IARC) - Agents Reviewed by the IARC Monographs", "International Chemical Secretariat (ChemSec) REACH SIN\* List (\*Substitute It Now!) 1.0", "US - Alaska Limits for Air Contaminants", "US - California Air Toxics ""Hot Spots"" List (Assembly Bill 2588) Substances for which emissions must be quantified", "US - California Occupational Safety and Health Regulations (CAL/OSHA) - Hazardous Substances List", "US - California Permissible Exposure Limits for Chemical Contaminants", "US - California Proposition 65 - Carcinogens", "US - California Proposition 65 - No Significant Risk Levels (NSRLs) for Carcinogens", "US - California Toxic Air Contaminant List Category V", "US - Connecticut Hazardous Air Pollutants", "US - Hawaii Air Contaminant Limits", "US - Idaho - Limits for Air Contaminants", "US - Maine Chemicals of High Concern List", "US - Michigan Exposure Limits for Air Contaminants", "US - Minnesota Hazardous Substance List", "US - Minnesota Permissible Exposure Limits (PELs)", "US - New Jersey Right to Know Hazardous Substances", "US - Oregon Permissible Exposure Limits (Z1)", "US - Pennsylvania - Hazardous Substance List", "US - Rhode Island Hazardous Substance List", "US - Tennessee Occupational Exposure Limits - Limits For Air Contaminants", "US - Vermont Hazardous Constituents", "US - Vermont Permissible Exposure Limits Table Z-1-A Final Rule Limits for Air Contaminants", "US - Vermont Permissible Exposure Limits Table Z-1-A Transitional Limits for Air Contaminants", "US - Washington Class A toxic air pollutants: Known and Probable Carcinogens", "US - Washington Dangerous waste constituents list", "US - Washington General Occupational Health Standards - List of Carcinogens", "US - Washington Permissible exposure limits of air contaminants", "US - Wyoming Toxic and Hazardous Substances Table Z1 Limits for Air Contaminants", "US ACGIH Threshold Limit Values (TLV)", "US ACGIH Threshold Limit Values (TLV) - Carcinogens", "US CERCLA Priority List of Hazardous Substances", "US Clean Air Act - Hazardous Air Pollutants", "US Department of Transportation (DOT) List of Hazardous Substances and Reportable Quantities - Hazardous Substances Other Than Radionuclides", "US DOE Temporary Emergency Exposure Limits (TEELs)", "US EPCRA Section 313 Chemical List", "US List of Lists - Consolidated List of Chemicals Subject to the Emergency Planning and Community Right-to-Know Act (EPCRA) and Section 112(r) of the Clean Air Act", "US National Toxicology Program (NTP) 11th Report Part A Known to be Human Carcinogens", "US NIOSH Recommended Exposure Limits (RELs)", "US OSHA Carcinogens Listing", "US OSHA Permissible Exposure Levels (PELs) - Table Z1", "US RCRA (Resource Conservation & Recovery Act) - Appendix IX to Part 264 Ground-Water Monitoring List 1", "US RCRA (Resource Conservation & Recovery Act) - Hazardous Constituents - Appendix VIII to 40 CFR 261", "US RCRA (Resource Conservation & Recovery Act) - List of Hazardous Inorganic and Organic Constituents 1", "US RCRA (Resource Conservation & Recovery Act) - Phase 4 LDR Rule - Universal Treatment Standards", "US Toxic Substances Control Act (TSCA) - Inventory"

**C.I. Solvent Orange 3, base (CAS: 495-54-5) is found on the following regulatory lists;**

"Canada Domestic Substances List (DSL)", "US Toxic Substances Control Act (TSCA) - Inventory"

## Section 16 - OTHER INFORMATION

### LIMITED EVIDENCE

- May produce discomfort of the eyes\*.
- \* (limited evidence).

### Denmark Advisory list for selfclassification of dangerous substances

Substance CAS Suggested codes C.I. Solvent Orange 3, base 495- 54- 5 Xn Mut3; R68

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- Classification of the mixture and its individual components has drawn on official and authoritative sources as well as independent review by the Chemwatch Classification committee using available literature references.



A list of reference resources used to assist the committee may be found at:  
[www.chemwatch.net/references](http://www.chemwatch.net/references).

■ The (M)SDS is a Hazard Communication tool and should be used to assist in the Risk Assessment. Many factors determine whether the reported Hazards are Risks in the workplace or other settings. Risks may be determined by reference to Exposures Scenarios. Scale of use, frequency of use and current or available engineering controls must be considered.

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