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USE and ASSESSMENT OF MARKER DYES USED WITH HERBICIDES

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Task No. **10**
USDA Order Nos. **43-3187-7-0408**
USDA Contract No. **53-3187-5-12**

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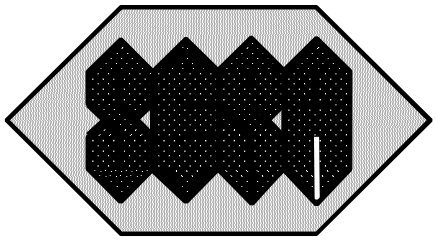

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ACRONYMS, ABBREVIATIONS, AND SYMBOLS

a.e.	acid equivalents
a.i.	active ingredient
AEL	adverse-effect level
ACGIH	American Conference of Governmental Industrial Hygienists
APHIS	Animal and Plant Health Inspection Service
ATSDR	Agency for Toxic Substances and Disease Registry
bw	body weight
BUN	blood urea-nitorgen
cm	centimeter
2,4-D	dichlorophenoxyacetic acid
DEA	Drug Enforcement Administration
EIS	environmental impact statement
F	female
FS	Forest Service
g	gram
GC	gas chromatography
HHRA	human health risk assessment
IARC	International Agency for Research on Cancer
kg	kilogram
L	liter
lb	pound
LC_{50}	lethal concentration, 50% mortality
LD_{50}	lethal dose, 50% mortality
LOAEL	lowest-observed-adverse-effect level
m	meter
M	male
mg	milligram
mg/kg/day	milligrams of agent per kilogram of body weight per day
mL	milliliter
MS	mass spectrometry
MW	molecular weight
NOAEL	no-observed-adverse-effect level
NOEL	no-observed-effect level
ppm	parts per million
R.E.D.	re-registration eligibility document
RfD	reference dose
U.S. EPA	U.S. Environmental Protection Agency
USDA	United States Department of Agriculture
>	greater than
≥	greater than or equal to
<	less than
≤	less than or equal to
=	equal to
≃	approximately equal to

1. INTRODUCTION

The U.S. Drug Enforcement Administration (DEA) is finalizing a Supplement to the Environmental Impact Statements (EISs) for the *Cannabis* Eradication program in the contiguous United States and Hawaii. The supplemental EIS is an update to the DEA's 1985 and 1986 EISs (DEA 1985,1986). Like the 1985 and 1986 EIS, the supplemental EIS is prepared in cooperation with the United States Department of Agriculture (USDA).

In previous EISs (DEA 1985 and 1986), the DEA ruled out the use of dyes or markers:

> *Numerous interagency task forces have investigated various types of dyes that could be used to mark potentially contaminated MMmarijuana ... Finding a workable marker has proven to be a difficult task. It is estimated that research first to find an effective marker and then to test its toxicity would cost more than $3 million and would not be completed for more than 3 years.* [DEA 1986, p. 2-7]

Various dyes are used, however, in current DEA programs (section 2). The dyes are considered necessary in selective or broadcast herbicide applications to allow the applicator to verify that the herbicide formulation was applied to the intended target. Furthermore, dyes discolor the targeted *Cannabis* plants making them unsuitable for use or marketing.

The supplemental EIS supports the use of two dyes: Fluorescent Red Liquid Concentrate and Hi-Light Blue. Another dye, Colorfast Purple, was used in some DEA sponsored programs but is not explicitly considered in the update document.

As the quotation above suggests, selecting a dye to use as a herbicide marker is a complex and potentially expensive undertaking. Nonetheless, the DEA decided to explore the use of alternative dyes as an adjunct to the two dyes covered under the supplement to the EIS.

The primary purpose of this report is to provide information that may be used to identify commercially available marker dyes for use with herbicides, particularly 2,4-D, glyphosate, and triclopyr, used by DEA in the eradication of marijuana:. Although the primary focus of this review is marker dyes for the eradication of marijuana, information that might apply to marking other types of vegetation is provided.

After an exhaustive literature search, it is clear that there is no published information regarding the use of marker dyes with herbicides. Moreover, the manufactures of the dyes and the suppliers of the herbicides do not make recommendations concerning the use of marker dyes. Through personal communication, it became clear that users of the dyes and not the manufacturers or suppliers usually determine the compatibility of a dye with a herbicide. The users also determine the efficacy of the dye for the a particular application. Consequently, this report attempts to summarize most of the essential factors that should be considered when assessing the compatibility and efficacy of different types of dyes over a broad range of applications (section 3). In addition, several specific dyes are used as markers in various applications by the USDA/Forest Service. These dyes may be considered alternatives to the dyes used now by DEA. Specific information regarding these dyes is summarized in section 4.

In addition to compatibility and efficacy issues, the potential human health effects of the dyes are of concern to the DEA. As summarized in the supplemental EIS, one of the agents in Fluorescent Red Liquid Concentrate is Rhodamine B, a compound shown to be carcinogenic to experimental mammals. Information about the toxicity of Rhodamine B, taken largely from the update to the EIS, as well as the toxicity of other potentially hazardous agents found in some commercial dyes are summarized in section 5.

2. CURRENT PRACTICE

The supplemental EIS indicates that the DEA may use the herbicides, glyphosate, 2,4-D, and triclopyr, in its programs involving the eradication of marijuana. Glyphosate is used in both Hawaii and Oklahoma, and 2,4-D is used in South Dakota. Triclopyr is not used currently in DEA sponsored programs involving the eradication of marijuana, but may be used in future DEA programs.

The DEA has used two dyes with commercial formulations of glyphosate. In program in Hawaii, Fluorescent Red Liquid Concentrate is added to a Rodeo/surfactant mixture. In program in Oklahoma, Colorfast Purple has been used with a Roundup Pro/surfactant mixture.

Fluorescent Red Liquid Concentrate is a dye formulation that contains Basic Violet 10, also known as Rhodamine B, as well as acetic acid, each at a concentration of 10% (Formulabs 1988). Basic Violet 10 is a xanthine derivative. The physical and chemical properties and structure of Basic Violet 10 are provided in appendix 1.

Basic Violet 10, also know as D&C [Drug and Cosmetic] Red No. 19, was once but is no longer approved as a cosmetic colorant in the United States (CTFA 1991). In the Hawaii program, each gallon of the applied mixture contains 0.2 liquid ounces of Fluorescent Red Liquid Concentrate along with 1 ounce of Rodeo and 0.2 liquid ounces of a surfactant (Terlep 1997). As indicated in the supplemental EIS, the mixture is applied as a directed aerial foliar spray.

Information regarding the total amount of herbicide/dye mixture typically applied during the course of 1 day is not available. On 1 day of an operation conducted during September 1996, 4600 plants were treated with 32 gallons of a glyphosate mixture applied by two helicopters, which amounts to approximately 0.007 gallons of the formulated mixture/plant. During the September 1996 spray operation, a total of 480 gallons of the mixture was used. Thus, the total amount of herbicide mixture applied was 15 lbs a.e. [0.03125 lbs a.e./gallon of mixture • 480 gallons of mixture] of glyphosate (a.e.) and 96 ounces or 3 quarts of both the surfactant and the dye.

In Oklahoma, ground equipment is used to apply Roundup Pro as a mixture with Surf King Plus surfactant and Colorfast Purple dye. Colorfast Purple is a commercial dye product formulated by Becker Underwood. The concentrations of the various constituents, which include Basic Violet 3 Dye, as the colorant, and dipropylene glycol and acetic acid, are considered proprietary (Hren 1997). The structure and a summary of the chemical and physical properties of Basic Violet 3 are provided in appendix 1. The CAS number specified on the Material Safety Data Sheet (MSDS)for Colorfast Purple is 67939-65-5 (Becker-Underwood, Inc.S 1997). This number refers to the acetate salt of Basic Violet 3. Most of the information about the potential toxicological effects of Basic Violet 3 (section 5.2) is attributed to the chloride salt [CAS No. 548-62-9], which is commonly referred to as Gentian Violet or Crystal Violet.

In the DEA program for Oklahoma, 1 gallon of Roundup Pro (3 lbs a.e.) is mixed with 50 gallons of water. One pint (16 liquid ounces) of the surfactant is added to this mixture along with 3 ounces of dye (Higbie 1997). During 1996, a total of 2500 gallons of the mixture was applied. This quantity amounts to 150 lbs a.e. of glyphosate, 6.25 gallons of the surfactant, and about 1.2 gallons of the dye formulation.

In applications that employ 2,4-D, only one dye, Hi-Light Blue, is used. Currently, this herbicide dye combination is used only in the DEA program for South Dakota. The ingredients in Hi-Light Blue are considered proprietary. None of the ingredients are listed as hazardous by SARA, and the dye contains no toxic chemicals under section 313 of Title III and 40 CFR 372. The dye used in Hi-Light Blue is commonly used in toilet bowl cleaners and as a colorant for lakes and ponds (Hren 1997). As discussed in section 4, blue dyes used as vegetation markers usually contain Acid Blue 9. The chemical and physical properties and structure of the dye are provided in appendix 1. Again, because the ingredients of Hi-Light Blue are considered proprietary, it is not indisputable that Acid Blue 9 is the colorant used in Hi-Light Blue.

In the DEA program for South Dakota, 2 quarts of the 2,4-D formulation (1.9 lbs. a.e.) is mixed with 100 gallons of water to give a solution of 0.019 lbs 2,4-D a.e./gallon. The dye is added at a concentration of 32 liquid ounces/100 gallons or 0.32 ounces/gallon. The 100 gallon mixture is applied to 1 acre (i.e., an application rate of 1.0 lbs a.e./acre). This application rate approximates the 2,4-D application rate recommended for the treatment *Cannabis* plants that are 19-24 inches high (Eaton 1972).

3. GENERAL CONSIDERATIONS

3.1. DEFINITIONS

Certain factors must be taken into consideration when determining what dye to choose as a vegetation marker (or for almost any other application). The first consideration is whether to use a dye, which is an organic colorant ***soluble*** in solvents and polymers, or a pigment, which is an inorganic/organic colorant ***insoluble*** in solvents or polymers. Furthermore, dyes generally offer higher color strength and produce very transparent colors, while pigments can be transparent or opaque. Overall, pigments have better fastness properties than dyes, especially lightfastness (i.e., pigments fade slowly in light) [BASF Corporation no date(a)].

Important factors to consider when matching dye properties with end use requirements, include solubility, compatibility, fastness properties, and price [BASF Corporation no date (a)]. To be most effective, a dyestuff must be soluble in the system in which it is used (e.g., water, solvents, oils, waxes and polymers). In addition, a dyestuff must be compatible with other components in the formulation. For example, an anionic (acid) dye should not be used in the same formulation as a cationic (basic) dye even though they are both water soluble dyes. Mixing incompatible dyes generally results in precipitation of the dye. The fastness or end use requirement of the dye also must be considered. Factors such as lightfastness, acid/base resistance, heat stability, etc. vary with classes of dyestuffs. For example, both basic and metal-complex solvent dyes are soluble in alcohols; however, the lightfastness of basic dyes is poor while the lightfastness of metal-complex dyes good. Finally, the cost of the dye must coincide with the end use application. For example, when using an alcohol based ink with minimal lightfastness requirements, it is better to use a lower priced basic dye instead of a more expensive solvent dye. Some other factors to consider in selecting a marker dye include ease of availability (some dyes are more difficult to manufacture and thus not readily available) and non-staining chemistry (whether the dye stains skin, clothes, etc. of the person applying the marker) (McClintock 1997).

3.2. CLASSES OF DYES

Dyes can be classified according to chemical structure or according to their usage or application. Dye chemists usually classify dyes according to chemical structure (i.e., azo dyes, anthraquinone dyes, and phthalocyanine

dyes), while dye users or technologists usually classify dyes according to their usage or application (e.g., reactive dyes for cotton and disperse dyes for polyester). Often times, both classifications are used (e.g., a phthalocyanine reactive dye for cotton and an azo disperse dye for polyester) (Gregory 1993).

Dye classification by usage or application is the principal method adopted by the *Colour Index* (The Colour Index 1971). The *Colour Index* assigns CI generic names to commercial dyes. The CI name is defined as "a classification name and serial number which when allocated to a commercial product allows that product to be uniquely identified within any *Colour Index* Application Class." This designation makes it possible to classify commercial dyes according to the chemical constitution of their essential colorant. That is, commercial dyes are given the same CI generic name if the chemical constitution of their essential colorant is the same. The *Color Index* does not claim, however, that preparations listed under the same CI generic name have identical application fastness or toxicological properties. Moreover, it should not be assumed that one commercial dye can replace another in every respect (Glover 1993).

There are many kinds of dyes, including acid dyes, basic dyes, direct dyes, disperse dyes, reactive dyes, solvent dyes, sulfur dyes, and vat dyes, which are characterized by their distinct chemical and physical properties (Gregory 1993, Glover 1993). Acid dyes are water-soluble anionic dyes, usually containing sulfonic acid groups or carboxylic acid groups, that have a high affinity for wool, other protein fibers (silk), and polyamides (modified acrylics). The lower the pH of the solution, the more rapid the dyeing process. Chemically, the acid dyes consist of azo (including preformed metal complexes), anthraquinone, and triarylmethane compounds with a few azine, xanthene, ketone imine, nitro, nitroso, and quinophthalone compounds.

Basic dyes, sometimes referred to as cationic dyes, are usually the salts of organic bases where the cation form of the molecule has the color. Basic dyes are water soluble and yield colored cations in solution. The principal chemical classes are diazahemicyanine, triarylmethane, cyanine, hemicyanine, thiazine, oxazine, and acridine.

Direct dyes are water-soluble anionic dyes, containing sulfonic acid groups, which have a high affinity for cellulosic fibers. Most of the dyes in this class are azo compounds with some stilbenes, phthalocyanines, and oxazines.

Disperse dyes are substantially water-insoluble nonionic dyes . They are the most important class of dye for dyeing hydrophobic synthetic fibers such as polyester and acetates.

Reactive dyes form a covalent bond with the fiber. A marked advantage of reactive dyes over direct dyes is that their chemical structures are much simpler, their absorption spectra show narrower absorption bands, and the dyeings are much brighter. The principle classes of reactive dyes are azo, triphendioxazine, phthalocyanine, formazan, and anthraquinone.

Solvent dyes are water-insoluble dyes devoid of polar solubilizing groups such as sulfonic acid, carboxylic acid, or quaternary ammonium. They are used to color plastics, gasoline, oils, and waxes. Solvent dyes are predominantly azo and anthraquinone; however, some phthalocyanines and triarylmethane dyes also are used.

Sulfur dyes are complex molecules containing sulfur obtained from the reaction between selected organic intermediates such as 4-aminophenol or *p*-phenylenediamine and molten sulfur or polysulfide. The actual structures of sulfur dyes are unknown, but it is assumed that they possess sulfur-containing heterocyclic rings. Although they are a small group of dyes, the low cost and good washfastness properties of the dyeings make this class important from an economic standpoint.

Vat dyes are water insoluble. They are formed by the conversion of an insoluble, complex, polycyclic molecule, based on the quinone structure, into a soluble leuco (white/clear) form by treatment with alkaline-reducing agents. The leuco form is absorbed onto the medium (usually cellulose) and then reconverted *in situ* to the colored insoluble pigment form, which is trapped within the fiber. The principal classes of vat dyes are anthraquinone and indigoid. This class of dyes is no longer commercially important.

3.3. USE OF DYES IN AGRICULTURAL INDUSTRIES

The three main agrochemical industries that use dyes to color agricultural chemicals or to identify agricultural chemicals by color include the fertilizer industry, the crop protection industry, and the seed dressing industry. Fertilizers are colored to distinguish their different qualities and to avoid errors in application. Coloring crop protection agents (e.g., insecticide and fungicides) helps to distinguish treated areas from untreated areas. In addition, the use of color is intended to promote safety in handling preparations. The purpose of coloring seed dressings is to avoid confusion and to prevent the seed from being used as fodder.

Coloring pesticides or herbicides often involves mixing dry powder formulations of the agents with chromatic pigments. Milori blue is the most widely used pigment, particularly with viticultural fungicides, but other pigments that are used include Heliogen Blue, Lithol Rubine, and Sico Fast Orange. If fungicide powders containing Pigmosol® preparations (pigments) are stirred into water, the color develops rapidly and the spray assumes an intense hue. Examples of products for this purpose are Pigmosol® Blue and Pigmosol® Orange.

On the other hand, crop protection agents can be colored before drying and grinding (i.e., while moist) using water-soluble dyes. Some of the available dyes include Basonyl® Violet, Basonyl® Red, Basacid® Orange, Basacid® Red, and Basacid® Blue [BASF Corporation no date(b)]. Basonyl® dyes are cationic dyes readily soluble in alcohols, glycol ethers, and water. They have high strength and brilliance. Basacid® dyes, available in liquid and powder form, are readily water-soluble anionic dyes suitable for coloring crop protection agents, fertilizers, industrial cleaners, antifreeze, wood preservatives, matches, and inks (BASF Corporation 1995).

Solvent dyes are used to color oily pesticide solutions. For example the BASF Corporation‘s Sudan® line of dyes, particularly Sudan® Blue, is used to color insecticides [BASF Corporation no date (b)]. As summarized in appendix 2, only one solvent dye, BAS-OIL Red® produced by Becker Underwood, was specifically identified as a candidate for use with oil-based herbicide formulations. As indicated in appendix 2, this dye contains a mixture of different solvent reds. The components of this oil-soluble colorant are proprietary. An extensive literature search provided information on 10 solvent red chemicals. These include CI. Solvent Red 1, Solvent Red 27, Solvent Red 5, Solvent Red 49, Solvent Red 72, CI Solvent Red 80, Solvent Red 44, Solvent Red 19, CI Solvent Red 24, and Solvent Red 23. Any number of these solvent red dyes might comprise Becker-Underwood’s BAS-OIL Red®.

According to an MSDS sheet obtained from the Vermont SIRI MSDS website (http://siri.org/), EI Dupont produces CI Solvent Red 164. The major components for CI Solvent Red 164 include xylene (35%), ethyl benzene (6.7%), benzene (<0.35%), and 2-napthtalenol [(phenylazo) phenyl]-azo alkyl derivatives (65%). The alkyl derivatives of azo benzene azo naphthol are what constitute the dye portion of CI Solvent Red 164. According to the MSDS, CI Solvent Red 164 is a dark red liquid with an aromatic hydrocarbon odor. The properties of the dye include negligible water solubility, a vapor pressure of 5.1 mm Hg at 68°F, and a composition of 33% volatiles by weight volume.

Although most of the non-toxic markers/indicators identified are acid dyes, depending on the chemical formulation of the crop protection agent, it may be desirable to use a basic dye instead. For instance,

sometimes, the color strength of a particular basic dye may be better than that of a similar acid dye. Further considerations regarding the choice of an acid dye or a basic dye include the dye color, the color strength, the dye stability over time, and the compatibility of the dye with a particular crop protection agent. Generally, it is a matter of trial and error to determine the most suitable dye for a given purpose.

4. DYES AS MARKERS/INDICATORS ON VEGETATION

Information about the use of commercial dyes as vegetation makers is summarized in Table 1. The list of dyes was compiled from information about the dyes used by the USDA Forest Service as markers for vegetation (Mistretta 1997) from information provided by the manufacturers and suppliers of dyes.

Most available markers and indicators are green and blue, and a high percentage of them are used for non-industrial purposes, like golf courses (McClintock 1997). The use of indicators on golf courses is predominantly cosmetic. Using a green indicator to spray the course with pesticides accentuates the green grass, making it look robust and healthy. Green indicators also are applied to courses during the winter months in the South when the grass is not dead but an unsightly brown. Blue indicators and dyes are frequently used to color ponds on golf courses to yield a more pronounced color.

An MSDS and product label were obtained for almost all of the markers/indicators, as indicated by a check mark on the table. Copies of the MSDS and product labels are included as supplementary information in appendix 2.

The major components of the marker/indicators are proprietary (Table 1). Generally, the known ingredients of the marker/indicators are those from red dyes and are listed on the MSDS. Basic Violet 10 is the same as Rhodamine B, and Basic Violet 3 is same as Crystal Violet. Crystal Violet is a purple dye (army green powder), similar in structure to rhodamine B, and has a high affinity

Table 1: Commercial dyes used as vegetation markers

Manufacturer/Supplier	Commercial Product	Dye Ingredients	Other Ingredients	MSDS[a]	Product Label[a]
Becker Underwood, Inc. 801 Dayton Ave Ames, IA 50010 800-232-5907 Fax: 515-232-5961	Hi-Light™ Blue Indicator	proprietary	NA	✓	✓
	Hi-Light™ WSP™ Industrial Strength Blue Indicator	proprietary	NA		✓
	Turf Mark® WSP™ Blue Spray Indicator	proprietary	NA	✓	✓
	Turf Mark® Green Liq Spray Pattern Indicator	proprietary	NA	✓	✓
	Turf Mark® Liquid	proprietary	NA	✓	✓
	BAS-OIL Red® (oil soluble colorant)	CI Solvent Red Mixture; proprietary	petroleum hydrocarbon; heavy naphthalenic distillate petroleum	✓	✓
	Spray Dye Red Conc	Basic Violet 10	acetic acid (39%)	✓	✓
	Spray Tracer Red	Basic Violet 10	acetic acid (16%)	✓	✓
	Spray Tracer Purple	Basic Violet 3	acetic acid (9.7%); dipropylene glycol	✓	✓
Cenex Land-O-Lakes Agronomy Co. St. Paul, MN 55164-0089 612-451-5151	Dynamark UV Blue Spray Indicator	proprietary	NA	✓	✓
	Dynamark UV Blue Spray Indicator, water soluble packets	proprietary	NA	✓	✓
	Dynamark UV Red Foam Colorant	Basic Violet 10	acetic acid (33%)	✓	✓

Table 1: Commercial dyes used as vegetation markers

Manufacturer/Supplier	Commercial Product	Dye Ingredients	Other Ingredients	MSDS[a]	Product Label[a]
	Dynamark UV Yellow Foam Colorant	proprietary	NA	✓	✓
DowElanco PO Box 681428 9330 Zionsville Rd Indianapolis, IN 46268 800-263-1196	Pathway* Specialty Herbicide	Dye and surfactant proprietary	2,4-D (20.9%); Picloram (5.4%); ethylene glycol; isopropanol; triisoprop-anolamine	✓	✓
Milliken Chemicals PO Box 1927 Spartanburg, SC 29304 864-503-6167 800-845-8502 Fax: 864-503-6186	Blazon® Blue Spray Pattern Indicator	proprietary	NA	✓	✓
	Bullseye® Blue Spray Pattern Indicator	proprietary	NA	✓	✓
Parkway Research Corp. 13802 Chrisman Road Houston, TX 77039 281-442-9821 Fax: 281-590-3353	Bigfoot®	proprietary	NA	✓	✓
Precision Laboratories, Inc. PO Box 127 Northbrook, IL 60065 847-498-0800 800-323-6280 Fax: 847-498-1176	Signal™ Spray Colorant (Blue)	proprietary	NA	✓	✓

[a] Indicates that the MSDS or product label are included in Appendix 4.
NA= Not available

for both cellulosic and proteinaceous substrates (Green 1990). According to the MSDS for Crystal Violet, ACGIH, NIOSH, and OSHA have not set exposure limits for the dye. As discussed in section 5, Rhodamine B and Basic Violet 3 (i.e.,Crystal Violet) are suspected carcinogens.

No information or recommendations are available from the manufacturers regarding the compatibility of dyes with herbicides (or pesticides in general). The compatibility of an herbicide with a particular indicator is usually determined by the consumer, who tests small portions of a dye indicator with an herbicide (using the manufacturers recommendations) and develops the best formulation for the intended use of the dye.

Most of the commercial indicators are blue. The actual dye used in indicator formulations is proprietary; however, most often a form of Acid Blue 9 is used. (McClintock 1997, Zullig 1997). A chemical profile of Acid Blue 9 is provided appendix 1, and an MSDS of Basacid® Blue NB 755 LM, BASF Corporation's equivalent of Acid Blue 9, is included in appendix 2.

Bullseye® spray pattern indicator should be differentiated from Blazon® spray pattern indicator from Milliken Chemicals. Bullseye® is a water soluble polymeric colorant, not a dye, and is non-staining to skin, clothing, and equipment. The product has greater color strength and was developed especially for use with herbicides, insecticides, and growth regulators in industrial wood control and forestry applications. Bullseye® is one of the few polymeric colorants available today. Blazon® does not have as strong a color strength as Bullseye® and is used primarily on turfs such as golf courses (i.e., non-industrial uses) (McClintock 1997).

The results of an extensive literature search indicate that Pathway* specialty herbicide from DowElanco is the only available herbicide that has a colorant already added. 2,4-D is the major component of Pathway*, which also contains some picloram. The herbicide is used primarily to control unwanted trees via cut surface treatments in forests, and on non-cropland areas, like fence rows, roadsides, and rights-of-way. The dye that is used in the herbicide mixture is not listed, but is obviously compatible. The appearance of the mixture is a blue-green liquid, suggesting that the dye is most likely an inert blue, an inert green, or a combination of both. In addition to the Pathway* specialty herbicide from DowElanco, some paraquat formulations (i.e., the Gramoxons) also come with a green dye. The dye is not identified on the label or MSDS, which means that it must be present at a concentration of less than 1% or that it contains-non hazardous chemicals.

Certain vegetation markers and indicators are no longer manufactured, including Exacto Chemical Company's Trail Blazer N/S (non-staining water soluble blue), Trail Blazer Basal Red 2000 (oil soluble red) and Trail Blazer Basal Blue 2000 (oil soluble blue), which were used by the USDA/Forest Service. Since small companies cannot compete with larger companies in the production of markers and either go out of business or merge with other companies, the turnover of marker producers is relatively quick, making it difficult to keep track of the markers that are available (McClintock 1997). In addition, certain companies have application patents (16) and this in turn limits the production of markers.

There are two general formulations available for many herbicides. The formulations are either water soluble or water insoluble or oil based (i.e., emulsifiable concentrates). Commercial formulations of 2,4-D and triclopyr are available as water soluble salt formulations as well as water insoluble ester formulations (i.e., emulsifiable concentrates). Nonetheless, information regarding the use of different dyes in both types of formulations is not available from manufacturers.

A supplemental literature search provided very little and only marginally relevant information about a tracer used to study spray distributions, which can be visualized in the dry state and recovered quantitatively from natural or artificial surfaces (Cooke and Hilsop 1993). The fluorescent water insoluble optical brightener Uvitex OB, also known as Helios (Ciba-Geigy), was determined to be stable and showed no detectable loss after a 1-hour exposure to strong sunlight, unlike fluorescein. The toxicity of the product is low, and the product is soluble in xylene-based emulsifiable concentrate (EC) pesticide formulations. Consequently, when Helios was diluted with water and dispersed in the non-aqueous phase together with the pesticide, it did not significantly alter the physical properties of the spray liquid. Moreover, Helios can be formulated as an emulsifiable concentrate; however, its addition to the pesticide mixture changed the physical properties of the spray (Cooke and Hilsop 1993). Due to its fluorescent nature, Helios has the potential to breakdown after prolonged periods of exposure to sunlight and may fade relatively fast. Therefore, although the tracer is soluble as an emulsifiable concentrate, it would probably be an unreliable vegetation marker.

Extensive literature searches and discussions with dye suppliers and manufacturers provided information on only one oil-soluble colorant, BAS-OIL Red®, which is available from Becker-Underwood. As discussed, the available literature indicates that Pathway* specialty herbicide from DowElanco is the only herbicide that has a colorant already added. Information regarding other ready-made herbicide/dye formulations is not available.

Many oil soluble dyes are used in the petroleum industry to mark gasoline; fluorescent oil-soluble dyes are used to detect fluid leaks in industrial automobiles or aircraft (Register 1997). The Sudan® line of dyes available from BASF Corporation are miscible with aromatics and have high color strength. Sudan S Orange 261 is used as a marking dye in heating oil and can be readily identified analytically (BASF Corporation 1995). Although the predominant use of the Sudan dyes are to mark gasoline, diesel oil, and lubricating greases, they have found uses in combination with crop protection agents. Sudan Blue 670 and Sudan Blue 672/673 Liquid can be used in marking oily insecticides (BASF Corporation 1995). There is no information regarding the compatibility of herbicides with Sudan dyes.

5. HAZARD EVALUATION

5.1. OVERVIEW

As summarized in Table 1, two colorants in commercially available dyes are listed as potentially hazardous. They are Rhodamine B and Basic Violet 3 (i.e.,Crystal Violet), both of which were shown to have carcinogenic activity in experimental mammals. These effects are considered quantitatively in the risk assessment (sections 5.2 and 5.3). The assessments are limited, however,

in that they apply only to current use patterns in DEA programs. If the use patterns were to change, either by increasing or decreasing the amount of dye applied or the amount of dye formulation handled, the risks would change in a linear manner.

The product labels and MSDS list several other components of the dyes described in section 4. Generally, the dye components are relatively common products (e.g., acetic acid and isopropanol) that are not considered hazardous. The toxicity of other dye components, like triisopropanolamine, are not well characterized, which leads to limited conclusions about the potential risk involving their use. More important, except for acetic acid, the amounts of the various constituents in the dye formulations are not specified. Hence, exposure assessments cannot be conducted and a complete assessment of potential hazard cannot be made. As discussed in section 6, limitations regarding the nature and availability of information about the various dye components constrains the risk characterization substantially.

5.2. RHODAMINE B.

5.2.1. Hazard Identification. As summarized in appendix 2, Rhodamine B is a colorant in some commercial dyes that might be used with herbicides. For instance, it is used in Fluorescent Red Liquid Concentrate, which is added to glyphosate in DEA sponsored programs in Hawaii (see section 2). Until the late 1980s, the FDA certified Rhodamine B stearate (D&C Red No. 19) as a color additive in cosmetics and drugs (IARC 1987). The certification was revoked; however, Rhodamine B free base (C.I. Solvent red 49) continues to be used as a dye for silk, cotton, wool, nylon, paper, inks, and various other materials (CTFA 1991). The literature contains references to the use of Rhodamine B as a tracing agent in water pollution studies (IARC 1987), but this use is not referenced in more recent studies.

The toxicology of Rhodamine B is relatively well studied. The acute LD_{50} for Rhodamine B in mice is approximately 900 mg/kg/day (IARC 1987). Similarly, the i.p. LD_{50} of Rhodamine B in rats ranges from approximately 60 to 140 mg/kg. The subchronic toxicity of Rhodamine B was investigated in several studies (IARC 1987). The lowest exposure level reported to cause adverse effects is from a multigeneration study using Charles River rats (Bio/Dynamics 1981a). A dietary concentration of 0.02% (200 mg/kg chow) caused early mortality in F_1 rats, an effect that was not observed at a dietary concentration of 0.002% (20 mg/kg chow). Assuming that rats consume food amounts equivalent to 5% of their body weight/day (U.S. EPA 1986), the NOAEL in this study would be 1 mg/kg/day with a corresponding LOAEL of 10 mg/kg/day.

In deriving the RfD for glyphosate (see section 3.3), the U.S. EPA classified 30 mg/kg/day as a LOAEL and based the RfD on a 10 mg/kg/day NOAEL for kidney damage. Both the NOAEL and LOAEL are from another multigeneration feeding study (Bio/Dynamics 1981b).

The potential carcinogenicity of Rhodamine B is also an endpoint of concern. Rhodamine B caused injection site sarcomas in rats when administered subcutaneously (Umeda 1956). In the study by Bio/Dynamics (1981a), an increase in granular cell brain tumors was observed in male rats exposed to a dietary level of 0.02% (200 mg/kg chow). In a standard 2-year feeding study, an increased

incidence in malignant hepatocellular tumors was observed among mice exposed to a dietary concentration of 0.1% (1000 mg/kg chow) (Bio/Dynamics 1981b).

5.2.2. Exposure Assessment. Exposure to Rhodamine B or any other colorant depends on the amount of the compound used as well as the extent of dermal absorption.

Information regarding the dermal absorption of Rhodamine B is not available in the literature. Based on an analysis of the dermal absorption of a series of organic compounds, Durkin et al. (1995) proposed the following relationship for an average daily absorption rate over a 5-day period:

$$\log AR = -0.004\ MW + 1.5$$

where AR is the percent absorption per day. The corresponding equation for a maximum daily absorption rate is:

$$\log AR = -0.005\ MW + 2.1$$

(Durkin et al. 1995, p. 73). The compounds used to develop the relationships include various steroids, pesticides, and industrially significant organic compounds; however, dyes were not included. As a class, dyes characteristically bind to proteins and other organic macromolecules. Consequently, the relationships cited above may overestimate the systemic absorption of dyes because the dyes may bind to the outer layers of the skin and be eliminated by exfoliation. Conversely, when dyes bind to the skin, the skin may function as a reservoir, which could result in systemic absorption. Without specific data regarding Rhodamine B, it is not clear how these competing processes will affect systemic absorption.

The molecular weight of Rhodamine B is 479 g/mole. Based on the above equations, the average percent absorption per day is 0.38% [$10^{-0.416}$]

$$(-0.004 \cdot 479) + 1.5 = -0.416$$

or 0.0038 day^{-1}. The estimated maximum percent absorption per day is 0.51% [$10^{-0.295}$]

$$(-0.005 \cdot 479) + 2.1 = -0.295$$

or 0.0051 day^{-1}. Because of the high degree of uncertainty associated with using these relationships for dyes, only the higher estimate is used in this risk assessment.

In the Human Health Risk Assessment (HHRA) in support of Supplemental EIS for the DEA marijuana eradication program, there is sufficient information regarding the current use of Fluorescent Red Liquid Concentrate with glyphosate to estimate an exposure rate for workers. In this program, an air crew handles approximately 3.2 lbs of Rhodamine B per day. Because data on Rhodamine B directly related to worker exposure is not available, the dose must be estimated by analogy to 2,4-D.

For 2,4-D, typical exposure rates are $3x10^{-5}$ ($3x10^{-6}$ to $3x10^{-4}$) mg/kg/lb a.i. for pilots and mixer/loaders (SERA 1993). As summarized in Durkin et al. (1995), the average absorption rate for 2,4-D over a 5-day period is 0.00048 $hour^{-1}$ or 0.012 day^{-1} or approximately 2.3 times the estimated rate for Rhodamine B [0.012 day^{-1} ÷ 0.0051 day^{-1} = 2.259]. Adjusting for this difference in estimated dermal absorption rates, the estimated exposure rate for air crews is $1.3x10^{-5}$ ($1.3x10^{-6}$ to $1.3x10^{-4}$) mg/kg bw/lb of Rhodamine B handled. Using the estimate of 3.2 lbs of dye/day, the estimated exposure rate for the air crews is $4.2x10^{-5}$ mg/kg/day with a range of $4.2x10^{-6}$ to $4.2x10^{-4}$ mg/kg/day.

An accidental exposure scenario is developed for spilling the herbicide dye mixture over the lower legs. In the DEA program in Hawaii, each gallon of the applied formulation contains 5.7 g of the dye, which in turn contains 10% Rhodamine B. Thus, the concentration of Rhodamine B in the mixture is 0.57 g/gallons, which is equivalent to approximately 150 μg/L or 0.15 mg/mL

$$0.57 \text{ g/gallon} \div 3.785 \text{ L/gal} = 0.15059 \text{ g/L}.$$

Thus, the amount of Rhodamine B adhering to the skin can be estimated as approximately 2.5 mg [16.56 mL · 0.15 mg Rhodamine B/mL]. The maximum absorption rate per day of 0.0051 day^{-1} corresponds to a rate of about 0.00021 $hour^{-1}$. Assuming that the skin is washed thoroughly after 1 hour, the absorbed dose can be estimated as 0.0000075 mg/kg or $7.5 \cdot 10^{-6}$ mg/kg

$$2.5 \text{ mg} \cdot 0.00021 \text{ h}^{-1} \div 70 \text{ kg}.$$

This estimate is only somewhat higher than the lower limit of the estimated absorbed dose associated with a typical aerial application (i.e., $4.2x10^{-6}$ mg/kg/day). Consequently, even though more severe or extreme accidental exposure scenarios could be constructed, the wide variation in the exposure estimates based on job categories seems to encompass accidental exposures, and no other exposure scenarios are developed for workers.

5.2.3. Dose-Response Assessment. As indicated in section 5.2.1, a standard 2-year feeding study in mice reports an increased incidence of hepatocellular tumors resulting from exposure to a dietary concentration of 0.1% (1000 mg/kg chow) (Bio/Dynamics 1981b). The mice were given Rhodamine B in the diet at concentrations of 0, 0.005%, 0.02%, and 0.1%. The response is female mice was greater than the response in males. The incidence of malignant liver tumors in the female mice was 0/115, 2/60, 5/60, and 14/60 in the 0, 0.005%, 0.02%, and 0.1% exposure groups, respectively, which is significantly greater than the response of the control group, using the Fisher exact test for both the mid ($p=0.004$) and high ($p=1.0 \cdot 10^{-7}$) exposure groups. The linearized multi-stage model (Faustman and Omenn 1996) was used to fit the concentration/response data. The Chi-square goodness of fit test yielded a p-value of 0.34, indicating that the model adequately fits the experimental data.

The lower bound on the dietary concentration that corresponds to a risk of 10^{-5} is $2.274 \cdot 10^{-6}$% or 0.02274 ppm. Assuming 30 g as a body weight for mice and taking a food factor of 0.13 (U.S. EPA 1986), the food concentration of 0.02274 ppm corresponds to a dose of approximately 0.003

mg/kg/day [0.02274 ppm • 0.13 mg/kg•ppm = 0.0029562 mg/kg]. Thus, the upper limit on potency for mice is $3.3 \cdot 10^{-3}$ $(mg/kg/day)^{-1}$ [$10^{-5} \div 0.003$ mg/kg/day]. Using the 3/4 power of the body weight ratios for extrapolating dose (U.S. EPA 1995a), the estimated human q_1^* is $22.9 \cdot 10^{-3}$ [$3.3 \cdot 10^{-3}$ $(mg/kg/day)^{-1} \cdot (70/0.03)^{0.25}$] or, rounding to one significant digit, $2 \cdot 10^{-2}$ $(mg/kg/day)^{-1}$.

5.2.4. Risk Characterization. Based on the estimated occupational exposure of 4.2×10^{-5} (4.2×10^{-6}-4.2×10^{-4}) mg/kg/day and the cancer potency estimate of $2 \cdot 10^{-2}$ $(mg/kg/day)^{-1}$, the estimated cancer risk—assuming a lifetime exposure—is $8 \cdot 10^{-7}$ with a range of $8 \cdot 10^{-8}$ to $8 \cdot 10^{-6}$. These values overestimate risk because they assume lifetime exposure. Various adjustments can be made, assuming that the total average daily dose is the determining factor in estimating risk (U.S. EPA 1995a). For example, if the total average daily dose is based on the assumptions that the herbicide is applied over a 5-day work week, 4 weeks/year and that the exposed workers have a 40-year career over a 70-year life span, the adjustment factor applied to the cancer potency factor would be 0.031 [5/7 days • 4/52 weeks • 40/70 years = 0.031] and the estimated lifetime risk would be $2 \cdot 10^{-7}$ with a range of $2 \cdot 10^{-8}$ to $2 \cdot 10^{-6}$.

Although somewhat arbitrary, the proposed adjustments are conservative. It is unlikely that one worker would apply the dye consistently for 4 weeks/year over a 40-year period. Risks using other exposure assumptions can be estimated by time-weighted averaging of the dose. For example, risks assuming an exposure of 8 weeks/year over a 30-year period would be based on an adjustment factor of 0.047 [5 days/7 week • 8/52 weeks • 30/70 years = 0.047096].

5.3. BASIC VIOLET 3.

5.3.1. Hazard Identification. Basic Violet 3 is the colorant used in Colorfast Purple. Colorfast Purple is a dye used with glyphosate in the Oklahoma *Cannabis* eradication program sponsored by the DEA. As indicated in appendix 2, Colorfast Purple is also a component in several other dye formulations that could be used as markers for vegetation.

Basic Violet 3 was used as a topical antimicrobial agent (CTFA 1991), as an antifungal agent (Hall and Hamilton 1982), and as a treatment for vaginal infections (Buttar et al. 1990, Hoag and Steiner 1983, Knowles et al. 1994) and oral infections (Nagel 1995). In addition, the dye is used as a laboratory reagent and stain (Thomas and MacPhee 1984) and as a colorant in master sheets for copiers (Halton 1983). Furthermore, it was proposed for use as a marker for industrial waste water (Bowman et al. 1982).

The toxicity of Basic Violet 3 is relatively well studied. Although the dye caused point mutations in bacterial species [TA-97 and TA-100], there was no clear activity in Chinese Hamster Ovary (CHO) cells (Aidoo et al. 1990). Base-pair substitution mutations were demonstrated in bacteria strain TA-1535 (Bonin et al. 1981). This dye also was characterized as a co-mutagen (Ferguson and Baguley 1988). The mutagenic activity of Basic Violet 3 may be enhanced by sunlight (Levin et al. 1982) and by animal metabolism (Thomas and MacPhee 1984). This dye was used as a positive control in the study of chemical mutagens by Krishnaja and Sharma (1995).

In a standard teratogenicity assay using CD rats, a dose of 10 mg/kg/day caused signs of maternal toxicity as well as various skeletal malformations in the fetuses. At doses that caused only mild signs of maternal toxicity (5 mg/kg/day) or no maternal effects (2.5 mg/kg/day), malformations were not observed (RTI 1982). In rabbits, doses as high as 2 mg/kg/day did not induce teratogenic effects, despite evidence of marked maternal toxicity (Wolkowski-Tyr et al. 1983). *In vitro,* concentrations of 50-250 µg/L caused mortality and/or an inhibition of cell cleavage in mouse embryos. The effects were not observed at exposure concentrations of 10 µg/L (Buttar et al. 1990).

The chronic toxicity and carcinogenicity of Basic Violet 3 was tested in mice (Littlefield et al. 1985) and rats (Littlefield et al. 1989). Marked carcinogenic activity was observed in mice, and this study serves as the basis for the quantitative cancer risk assessment for this compound (Littlefield et al. 1985). In rats, there is an indication that the dye accelerates the development of leukemia; however, the effect is less remarkable than that observed in mice (Littlefield et al. 1989).

Turkeys exposed to Basic Violet 3 in drinking water contracted occlusive laryngotracheitis (Clark et al. 1993). A marker solution containing the dye, dihydroxyacetone, and acetone was associated with contact dermatitis, although the dye itself did not cause an allergic reaction (Cox et al. 1989). In patch tests, concentrations between 0.01% and 5% of Crystal Violet lactone [CAS 1552-42-7] used in carbonless copy paper were associated with the development of contact dermatitis (Shehade et al. 1987).

5.3.2. Exposure Assessment. As with the exposure assessment for Rhodamine B, two types of exposures are modeled for workers, including exposures based on job categories and accidental exposures. Unlike the Rhodamine B dye (i.e., Fluorescent Red Liquid Concentrate), the amount of Basic Violet 3 in Colorfast Purple is considered proprietary and the formulator did not released the information for use in this risk assessment. For the purpose of making a crude comparison, it is assumed that the plausible amount of colorant (i.e., Basic Violet 3) in the dye formulation (i.e., Colorfast Purple) could range from 5% to 30%. For this exposure assessment, the amount of colorant is assumed to be 10%. The uncertainties with this estimate are discussed in the risk characterization for Basic Violet 3 (section 5.3.4).

As with the exposure assessment for Rhodamine B, these exposure assessments require estimates of dermal absorption rates. There is no information available about the dermal absorption of Basic Violet 3. The molecular weight of Basic Violet 3 is 408 g/mole. Based on the relationships developed by Durkin et al. (1995) (see section 5.2.2), the estimated maximum percent absorption per day is 1.1% [$10^{0.06}$]

$$(-0.005 \cdot 408) + 2.1 = 0.06$$

or 0.011 day^{-1}.

Like exposure to Rhodamine B, exposure to Basic Violet 3 is estimated by analogy to 2,4-D. For 2,4-D, typical exposure rates are $3x10^{-5}$ ($3x10^{-6}$ to $3x10^{-4}$) mg/kg/lb a.i. for pilots and mixer/loaders

(SERA 1993). As summarized in Durkin et al. (1995), the average absorption rate for 2,4-D over a 5-day period is 0.00048 $hour^{-1}$ or 0.012 day^{-1}, which is equivalent to the estimated dermal absorption for Basic Violet 3. Thus, the exposure rates for 2,4-D are applied directly and without modification for the Basic Violet 3 exposure assessment.

In the current DEA program in Oklahoma, each gallon of the applied mixture contains 0.02 gallons of Roundup Pro (i.e., 1 gallon of Roundup Pro per 50 gallons of water). This amount is equivalent to 0.08 lbs a.i. of glyphosate [0.02 gallons · 4 lbs a.i./gallon], which is in turn equivalent to 36 g [0.08 lbs • 453.6 g/lb] of glyphosate (a.i). The applied mixture also contains 3 ounces of dye per 50 gallons of the mixture or 0.06 ounces/gallon. This amount is equivalent to approximately 1.8 mL [0.06 liquid ounces • 29.5735 mL/liquid ounce] or 1.8 g, assuming a specific gravity of 1 g/mL. Using 10% as the estimated concentration of Basic Violet 3 in Colorfast Purple, the amount of Basic Violet 3 per gallon is approximately 0.18 g. Thus, the ratio of the dye to glyphosate (a.i.) is approximately 0.005 [0.18 g ÷ 36 g], which is notably less than the ratio of Rhodamine B to glyphosate [0.57 g dye ÷ 3.58 g glyphosate = 0.15].

For ground applications of 2,4-D, plausible estimates and ranges of exposure rates are $9.6x10^{-5}$ ($4.9x10^{-6}$ to $1.9x10^{-3}$) mg/kg/lb a.i. for roadside hydraulic spraying and $1.4x10^{-3}$ ($4.4x10^{-5}$ to $4.2x10^{-2}$) mg/kg/lb a.i. for directed foliar backpack applications (see Table 3-2 in SERA 1995). When a factor of 0.005 is used to relate the applied amount of glyphosate to the applied amount of dye, an application rate of 1.5 lbs a.i. glyphosate/acre corresponds to 0.0075 lbs dye/acre.

Boom spray operations may treat 10-20 acres/hour or 80-160 acres/day. Thus, at an application rate of 0.0075 lbs dye/acre, the amount of dye handled per day could range from 0.6 to 1.2 lbs/day. When the exposure rates for 2,4-D are used, the upper limit corresponds to a dose rate of $1.1 \cdot 10^{-4}$ ($5.9 \cdot 10^{-6}$ to $2.2 \cdot 10^{-3}$) mg/kg/day,

$$9.6x10^{-5} \text{ } (4.9x10^{-6} \text{ to } 1.9x10^{-3}) \text{ mg/kg/lb a.i.} \cdot \text{ } 1.2 \text{ lbs.}$$

Directed foliar backpack applications of 2,4-D are associated with exposure rates of $1.4x10^{-3}$ ($4.4x10^{-5}$ to $4.2x10^{-2}$) mg/kg/lb a.i. (see Table 3-2 in SERA 1995). Although these rates are substantially greater than those estimated for hydraulic spraying, backpack applicators usually treat only 0.25-1.0 acres/hour or 2-8 acres/day. Thus, at an application rate of 0.0075 lbs dye/acre, the amount of dye handled per day could range from 0.015 to 0.06 lbs/day. The upper limit based on 8 acres/day corresponds to a dose rate of $8.4 \cdot 10^{-5}$ ($2.6 \cdot 10^{-6}$ to $2.5 \cdot 10^{-3}$) mg/kg/day,

$$1.4x10^{-3} \text{ } (4.4x10^{-5} \text{ to } 4.2x10^{-2}) \text{ mg/kg/lb a.i.} \cdot \text{ } 0.06 \text{ lbs.}$$

Thus, the exposure rates for hydraulic sprayers and backpack applicators are comparable.

Although it is not plausible that the general public will be exposed to dyes used in direct aerial applications, exposure may occur as a result of broadcast or directed ground applications, primarily because the *Cannabis* treated in the ground applications may grow in ditches along roads or other

relatively accessible areas. Moreover, given the nature of broadcast applications, there is greater likelihood for inadvertent treatment of non-target vegetation (e.g., berries or other fruits).

There are no monitoring studies regarding residue levels of dye in vegetation after ground applications. Field applications of 1.5, 4.5, and 15 lbs of glyphosate (a.i)/acre were associated with residue levels of 442, 1210, and 4155 mg glyphosate/kg marijuana.(RTI 1984). For comparison, empirical relationships based on initial residues for many pesticides shortly after application by various methods suggest typical residue rates of 125 mg/kg·lb a.i./acre on leaves and leafy crops and extreme residue rates of 240 mg/kg·lb a.i./acre on range grass. For fruits, grains, and seed pods, the corresponding estimates are 1.5-12 mg/kg (Hoerger and Kenaga 1972). The residue rate monitored by RTI (1984) at the lowest application rate is equivalent to 294 mg/kg·lb a.i./acre,

$$442 \text{ mg/kg} \div 1.5 \text{ lbs a.i./acre}$$

which is relatively close to the extreme residue rate of 240 mg/kg·lb a.i./acre for range grass, which was provided by Hoerger and Kenaga (1972).

Thus, using the RTI (1984) rates for glyphosate, an application rate of 1.5 lbs/gallon would yield an initial glyphosate residue of 442 mg glyphosate (a.i)/kg of marijuana. Since, however, the dye is applied at a rate of 0.0075 lbs/acre, the residue on marijuana plants would be 1.47 mg dye/kg marijuana,

$$0.005 \text{ lbs day/lb glyphosate} \cdot 294 \text{ mg glyphosate (a.i)/kg.}$$

As discussed, fruits have much lower residues, typically 1.5-12 mg residue/kg fruit (Hoerger and Kenaga 1972). Thus, at an application rate of 0.0075 lbs dye/acre, the residues would range from 0.017 to 0.135 mg dye/kg fruit,

$$1.5 \text{ lbs a.i. glyphosate/acre} \cdot 0.0075 \text{ lbs dye/lb glyphosate} \cdot 1.5 \text{ to } 12 \text{ mg residue/kg fruit·lbs/acre.}$$

Using the same assumptions specified in the exposure assessment for glyphosate (see section 3.2.3.6), it is assumed that a 64 kg woman (U.S. EPA 1985) consumes 1 pound (0.454 kg) of contaminated berries. Hence, the estimated dose is $1.2 \cdot 10^{-4}$ mg/kg to $9.6 \cdot 10^{-4}$ mg/kg

$$0.017 \text{ to } 0.135 \text{ mg dye/kg fruit} \cdot 0.454 \text{ kg fruit} \div 64 \text{ kg.}$$

The plausibility of individuals consuming fruit marked with a dye is questionable. Moreover, it is extraordinarily implausible that individuals would consume or would have access to contaminated fruit over a substantial portion of their life span. Consequently, there is no reason to develop elaborate exposure scenarios involving the consumption of fruit contaminated with dye.

5.3.3. Dose-Response Assessment. As discussed in section 5.3.1, standard 2-year feeding studies were conducted in rats and mice (Littlefield et al. 1985 and 1989). The greatest degree of carcinogenic activity was observed in female mice (Littlefield et al. 1985). At daily dose levels of 0, 14, 37.5, and 71.4 mg/kg/day, the rates of hepatocellular carcinoma were 7/185, 5/93, 30/93, and 73/95. The linearized multi-stage model (Faustman and Omenn 1996) was used to fit the concentration/response data. The Chi-square goodness of fit test yielded a p-value of 0.42, indicating that the model adequately fits the experimental data.

The lower bound on the daily dose, which corresponds to a risk of $10^{-5,}$ is $1.962 \cdot 10^{-3}$ mg/kg/day. Thus, the upper limit on potency for mice is $5.1 \bullet 10^{-3}$ $(mg/kg/day)^{-1}$ [$10^{-5} \div 1.962 \cdot 10^{-3}$ mg/kg/day]. Using the 3/4 power of the body weight ratios for extrapolating dose (U.S. EPA 1995a), the estimated human q_1^* is $35.4 \bullet 10^{-3}$ [$5.1 \bullet 10^{-3}$ $(mg/kg/day)^{-1} \bullet (70/0.03)^{0.25}$] or $4 \bullet 10^{-2}$ $(mg/kg/day)^{-1}$, rounding to one significant digit,. Thus, it is estimated that the carcinogenic potency of Basic Violet 3 is about twice that of Rhodamine B.

5.3.4. Risk Characterization. Using the estimated dose rates for boom-spray workers, which is $1.1 \cdot 10^{-4}$ ($5.9 \cdot 10^{-6}$ to $2.2 \cdot 10^{-3}$) mg/kg/day and the cancer potency estimate of $4 \bullet 10^{-2}$ $(mg/kg/day)^{-1}$, the estimated cancer risk—assuming a lifetime exposure—is $4 \cdot 10^{-6}$, with a range of $2 \cdot 10^{-7}$ to $9 \cdot 10^{-5}$. For backpack applicators, the dose rates are $8.4 \cdot 10^{-5}$ ($2.6 \cdot 10^{-6}$ to $2.5 \cdot 10^{-3}$) mg/kg/day, which corresponds to cancer risks of $3 \cdot 10^{-6}$ ($1 \cdot 10^{-7}$ to $1 \cdot 10^{-4}$). The risks are estimated by multiplying the estimated dose rate by the estimated cancer potency of $4 \bullet 10^{-2}$ $(mg/kg/day)^{-1}$. Like the assessment of cancer risks associated with exposure to Rhodamine B, these values grossly overestimate risk because they are based on the assumption of lifetime exposure. Appying the same adjustment factor of 0.03 used in the Rhodamine B risk characterization, the maximum estimated lifetime risk is $3 \cdot 10^{-6}$

$$1 \cdot 10^{-4} \cdot 0.031$$

and the typical risk is about $9 \cdot 10^{-8}$ to $1 \cdot 10^{-7}$

$$3 \cdot 10^{-6} \text{ to } 4 \cdot 10^{-6} \cdot 0.031.$$

As discussed in section 5.3.2, the only plausible exposure scenario for members of the general public involves the consumption of contaminated fruits inadvertently sprayed during a broadcast ground application. The estimated dose levels of $1.2 \cdot 10^{-4}$ mg/kg to $9.6 \cdot 10^{-4}$ mg/kg, assuming they occur daily over a lifetime, correspond to risks of $5 \cdot 10^{-6}$ to $4 \cdot 10^{-5}$. The risk associated for a single exposure is adjusted by 0.000039, the reciprocal of the number days in a 70-year lifes pan [$70 \cdot 365 = 25{,}550$; $1/25{,}550 = 0.000039$]. Thus, the risk associated with consuming contaminated berries for 1 day is in the range of $2 \cdot 10^{-10}$ to $1 \cdot 10^{-9}$,

$$1.2 \cdot 10^{-4} \text{ mg/kg to } 9.6 \cdot 10^{-4} \text{ mg/kg} \cdot 0.04 \cdot 3.9 \cdot 10^{-5}$$

There is a linear relationship between the risk for multiple days of exposure and the risk of exposure for 1 day.

It is conceivable that human exposure to Basic Violet 3 may result from consumption of contaminated vegetation; however, one of the purposes of using the dye is to alert individuals to the fact that the vegetation was treated. Therefore, although the risk characterization takes into account this exposure scenario, the scenario is considered extreme rather than typical.

An additional source of uncertainty in the risk characterization for Basic Violet 3 is the lack of information regarding its level in the commercial dye, Colorfast Purple. As indicated in section 5.3.2, the amount of Basic Violet 3 in Colorfast Purple is considered proprietary. The exposure assessment (see section 5.3.2) is based on the assumption that Basic Violet 3 comprises 10% of Colorfast Purple. Consequently, risks associated with exposure to the dye could be as many as 10 times greater than those derived, if Colorfast Purple were to contain 100% Basic Violet 3. Thus, typical risks for workers could range from about $9 \cdot 10^{-7}$ to $1 \cdot 10^{-6}$, with an upper limit of $3 \cdot 10^{-5}$. For the general public, the risks associated with exposure for 1 day could range from $2 \cdot 10^{-9}$ to $1 \cdot 10^{-8}$. The assumption that Colorfast Purple contains virtually 100% Basic Violet 3 is not reasonable; consequently, calculations based on that assumption are provided as the upper limit of exposure in the absence of information regarding the amount of Basic Violet 3 in Colorfast Purple.

5.4. OTHER AGENTS IN DYE FORMULATIONS

As indicated in appendix 2, several other components may be present in various dye formulations, including acetic acid, dipropylene glycol and ethylene glycol, various petroleum products, isopropanol, and triisopropanolamine. This is a list of additives identified by the dye manufacturers and should not be considered comprehensive. Like the colorants in the dyes, the additives and adjuvants are considered proprietary. Most manufacturers and do not publicly disclose the identity of the agents unless the agent is classified as hazardous. Furthermore, even when manufacturers disclose the identity of additives and adjuvants in commercial formulations, they usually do not specify concentrations. Restrictions regarding the release of proprietary information about the components of the various dye formulations impedes the assessment of potential hazard significantly.

The only component that is identified and quantified is acetic acid. This compound is present at levels of approximately 10-33% in various dye formulations (appendix 2). Acetic acid may be classified as toxic because of its irritant effects. Like may organic acids, acetic acid may cause skin and eye irritation as a result of exposure to concentrated solutions. Prolonged contact with concentrated solutions may produce severe eye damage. Hence, the presence of acetic acid in Fluorescent Red Liquid Concentrate or other dye formulations might contribute to the irritant effects of a herbicide formulation. Nonetheless, acetic acid is not a constituent of concern in terms of systemic toxic effects. Acetic acid is a major component of vinegar and several other natural products and is on the Generally Recognized as Safe (GRAS) list (Kotsonis et al. 1996).

Similarly, propylene glycol is relatively non-toxic to mammals and is approved for use in foods, cosmetics, and pharmaceuticals. The compound was adequately tested for carcinogenicity, mutagenicity, and reproductive effects and no positive results were reported. As with acetic acid, propylene glycol is on the FDA's GRAS list (Synder and Andrews 1996).

Unlike propylene glycol, ethylene glycol and diethylene gylcol have well characterized toxicities (Synder and Andrews 1996). U.S. EPA (1997) derived an RfD of 2 mg/kg/day for ethylene glycol, based on a 2-year feeding study in mice and rats (DePass et al. 1986). The RfD was derived using a NOAEL of 200 mg/kg/day for mice, divided by an uncertainty factor of 100. Doses as high 1000 mg/kg/day ethylene glycol did not cause adverse effects in mice. In rats, however, doses of 1000 mg/kg/day were associated with increased mortality, neutrophil count, water intake, kidney hemoglobin and hematocrit, and chronic nephritis. The U.S. EPA does not propose an RfD for diethylene glycol. In a 2-year dietary study (Fitzhugh and Nelson 1946), diethylene glycol caused kidney effects in rats, which were consistent with the adverse effects of ethylene glycol.

Petroleum distillates represent an extremely complex class of chemicals (MacFarland et al. 1984). Although some components of kerosene are known to be carcinogenic to humans (e.g., benzene) kerosene is not classified as a carcinogen, and quantitative risk assessments have not been conducted on kerosene (ATSDR 1995). The toxicity of gasoline is related to the level of benzene in the gasoline (Snyder and Andrews 1996). It is not clear, however, that the petroleum derivatives used in dyes contain benzene. Many components in petroleum products also cause neurological effects. For example, the NOAEL for neurological effects in experimental mammals after exposure to kerosene for periods ranging from 14 days to 1 year is approximately 100 mg/m^3; the NIOSH TLV for petroleum distillates is 350 mg/m^3 (ATSDR 1995).

There is a large database on the toxicity of isopropanol to mammals, aquatic organisms, and other wildlife species. Much of this data are summarized by U.S. EPA (1995b) in the Reregistration Eligibility Decision (RED) document on aliphatic alcohols. The RED covers isopropanol as well as ethanol, both of which are classified as active ingredients in various commercial products including insecticides, ripeners, sterilants, medical disinfectants, and fungicides. At high doses, both ethanol and isopropanol (rubbing alcohol) can be toxic; however, under typical conditions of use, the U.S. EPA concluded that neither compound will pose: *unreasonable risks of adverse effects to humans or the environment* (U.S. EPA 1995b, p. v). Nonetheless, under the conditions of certain exposure scenarios, ethanol and isopropanol may result in potentially hazardous exposures:

> *The registered use of these aliphatic alcohols may result in high dermal and inhalation exposures during mixer/loader and applicator use of aliphatic alcohol products, especially when power sprayers are used. However, the risk from exposures to these active ingredients is considered to be incidental when compared to intentional human exposure* (U.S. EPA 1995b, p. 29).

In contrast to isopropanol, there is no information available on the toxicity of triisopropanolamine. As summarized in Clayton and Clayton (1994, p. 1157), a standard and reasonably comprehensive reference text in industrial hygiene, there are no published toxicity studies or hygienic standards for triisopropanolamine. Additional literature searches on MEDLINE and AGRICOLA, surveys of internet resources provided by the U.S. EPA and ATSDR, as well as an examination of other standard reference texts did not identify any relevant information about the toxicity of this compound.

6. SUMMARY AND CONCLUSIONS

There is extremely little information available to assist the DEA or other organizations in their efforts to select dyes to use as markers on vegetation. Although dyes are used extensively in many industrial and agricultural applications, their use is virtually unregulated and there is almost no guidance regarding the selection of dyes based on their efficacy or potential hazard.

The use of any agent—herbicides, dyes, surfactants, or other additives—may pose some level of human risk. As discussed in the supplemental EIS, the use of dyes may also have beneficial consequences. For example, dyes will discolor the treated vegetation, making it less likely that an individual will inadvertently or intentionally consume contaminated vegetation. Moreover, the use of dyes in a herbicide formulation could assist workers in limiting their exposure to the dye/herbicide formulation. In other words, the presence of a dye in the applied formulation will make it easier for workers and supervisors to recognize when exposure has occurred, which, in turn, could facilitate prompt remedial action.

Not withstanding these potential benefits, the colorants or other components in the dyes may pose additional risks to humans and wildlife. As noted in section 3, however, the assessment of these risks is severely limited by the proprietary nature of dye formulations. For most of the available dyes, neither the colorants nor adjuvants in the dye formulation are disclosed by the manufacturers. As reviewed by Levine (1996), this problem is general to the assessment of risks posed by all inerts in pesticide formulations. Unless the compound is classified as hazardous by the U.S. EPA, the manufacturer is not required to disclose its identity. This policy would not seriously impede the process of risk assessment if the regulation and classification of inerts involved rigorous testing comparable to those associated with active ingredients. That, however, is not the case. As discussed by Levine (1996), the U.S. EPA is increasing the testing requirements on new inerts; however, many of the inerts currently in use were not tested rigorously and their toxicity is not well characterized. Thus, when a colorant or other adjuvant in a dye formulation is not listed as hazardous and therefore not identified on the product label or MSDS (e.g., Appendix 2) it should not be concluded that the dye or adjuvant is not toxic.

The complexity of this situation is increased somewhat by the ways in which toxicity data are used to classify compounds as hazardous. As discussed, two of the colorants, Rhodamine B and Basic Violet 3 (i.e.,Crystal Violet), are carcinogens. None of the herbicides used by DEA are classified as carcinogens. Thus, this endpoint must be addressed explicitly in assessments regarding the use of these dyes as markers, as done in section 5.2 and 5.3. Other agents, such as acetic acid and isopropanol, are classified as hazardous and are listed on various product labels (see Table 1). Whether these agents pose a significant or substantial risk is far less clear. As discussed in section 5.4, many of these agents are common household commodities. Although any agent can be ‘toxic’ at very high dose levels, it is not clear whether the presence of these agents in dye formulations amounts to a substantial health risk.

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Supplemental Notes on Correspondence

On October 9, 1997 Michelle Pepling corresponded via telephone with Donald Gaylord from BASF Corporation (1-800-537-7390). Mr. Gaylord provided a brief overview of dyes and offered ideas of where to look within the dye industry for information concerning markers.

On October 17, 1997 Michelle Pepling went to BASF Corporation at 36 Riverside Ave Rensselaer, NY and talked with Dr. Charles Zullig and Jeffrey Moehler (1-800-537-7390). Dr. Zullig provided chemical information about the classes of dyes as well as the trends within the dye industry. Dr. Zullig also allowed the utilization of textual information, i.e., the *Colour Index*, that belonged to BASF. Jeffrey Moehler provided technical information for dyes and BASF dyes in particular. In addition, they both offered leads of dye companies to contact for more information. The Dye Lab at BASF in Rensselaer was also helpful in clarifying questions about dyes.

On October 21, 1997 Michelle Pepling corresponded via telephone with Miller McClintock from Milliken Chemical Company in Spartanburg, SC (864-503-2220). Mr. McClintock was able to provide general information concerning Milliken products. What was most useful was his information regarding trends within the spray indicator industry and what a consumer of indicators is looking for when purchasing an indicator.

8. GLOSSARY

anionic dye: A dye that has a negative charge.

anthraquinone dye: A dyes whose molecular structure is based on anthraquinone: The chromophore groups are =C=O- and =C=C=.

azo dye: Any of a broad series of synthetic dyes that have -N=N- as a chromophore group.

base out: “Basing out” is a chemical reaction undergone by the dye in the presence of high pH. Basic dyes are a color base dissolved in an acid. The acid gives the base its color, hence the pH must remain on the acidic side. When a basic dye reverts back to its color base it will fall out of solution since the color base is insoluble and thus the dye has no color value. Adding acid will dissolve the base giving the dye color again. Therefore, the basing out reaction is reversible (19).

cationic dye: A dye that has a positive charge.

chromophore: A chemical grouping which when present in an aromatic compound (the chromogen) gives color to the compound by causing a displacement of, or appearance of, absorbent bands in the visible spectrum.

fastness: Descriptive of a dye or pigment whose color is not impaired by prolonged exposure to light, steam, high temperature, or other environmental conditions. Inorganic pigments are normally superior in this respect to organic dyes.

fluorescein: Also known as uranine C. The disodium salt is a hygroscopic (absorbs moisture from air) orange-red powder. Yields an intense yellowish-green fluorescence in water. The fluorescence disappears when the solution is made acid, and reappears when the solution is again made neutral or alkaline.

flourescent dye: Dyes which when exposed to light fluoresce (i.e., adsorb shorter wavelength light and emit longer wavelength light). This property allows them to be detected at the ug/l and ng/l range using a fluorometer.

karst terrain: A landscape that exhibits irregularities in surface form caused by rock dissolution.

lightfastness: Descriptive of a dye or pigment whose color is not impaired by prolonged exposure to light. For example, a dye that has good lightfastness will fade slowly in light.

molori blue: Any of a number of the varieties of iron blue pigments, prepared by precipitating ferrous ferrocyanide from a solution of ferrocyanide and ferrous sulfate (13).

non-ionic dye: A dye that does not have a charge.

optical brighteners: Also known as fluorescent whitening agents. The are a colorless, flourescent organic compound that absorbs ultraviolet light and fluoresces in the blue region of the visible spectrum. The main commercial use is in laundry detergents and textile finishing.

pthalocyanine dye: Any of a group of benzoporphyrins that have strong pigmenting power, forming a family of dyes. The basic structure consists of four isoindole groups [$(C_6H_4)C_2N$] joined by four nitrogen atoms.

rhodamine WT: A highly fluorescent dye with the unique ability to absorb green light and emit red light. It exhibits exceptionally high tinctorial strength and a low tendency to stain silt, dirt, plants, and other suspended matter in fresh and salt waters.

It is used extensively to identify underground water flow patterns in waste-water treatment basins and in process liquid of industrial plants.

substantive: "Has a high affinity to"

tracer: A compound (usually dyes or salts) used to mark the course of a process. They are predominantly used for measuring, mapping, and monitoring water systems.

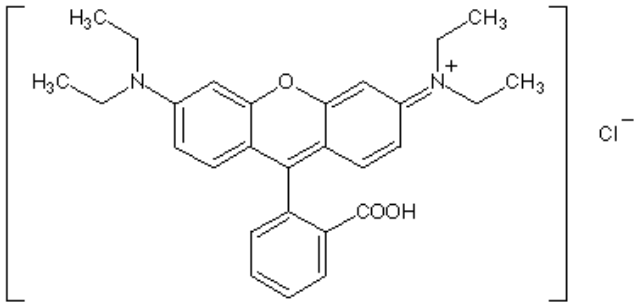
triarylmethane dye: Any of a group of dyes whose molecular structure involves a central carbon atom joined to three aromatic nuclei. The color is due in part to the aromatic rings and to the chromophore groups =C=NH and =C=N-.

triphenylmethane dye: Any of a group of dyes whose molecular structure is basically derived from $[(C_6H_5)_3CH_3]$. Many coal tar and synthetic dyes are of this class, including rosaniline, fuchsin, malachite green, and crystalline violet.

xanthene dye: A group of dyes whose molecular structure is related to that of xanthene. The aromatic $[C_6H_4]$ groups constitute the chromophore. Xanthene is the central structure of fluorescein, eosin, and rhodamine dyes.

Appendix 1
Summary of Chemical and Physical Properties of Some Commercial Dyes Used as Vegetation Markers

Rhodamine B



CAS Number:	81-88-9
Molecular weight:	479.02
Melting point (°C):	210-211°C (dec) (Aldrich, 1996) 165°C (basic anhydrous form) (IARC, 1978) 172-17 6°C (Chem. Inspect. Test Inst., 1992)
Density (g/cm^3):	-----
Vapor Pressure (mm Hg):	< 1×10^{-14} mm Hg at 25°C (MPBPVP, 1997)
Water Solubility:	12 g/L at 20-25°C (Baughman et al., 1993) 10 g/L (Chem. Inspect. Test Inst., 1992) 30-50 g/L (commercial product 80-90% pure; Green, 1990)
Henry's law constant:	< 1×10^{-14} atm-m^3/mole at 25°C (method of Meylan and Howard, 1991) < 1×10^{-15} atm-m^3/mole at 25°C (calculated from vapor pressure & water solubility)
pKa:	-----
Log K_{ow}:	1.90 - 2.00 (Chem. Inspect. Test Inst., 1992)
Dermal Permeability Coefficient:	5.53×10^{-5} cm/hr(estimated by method of USEPA, 1992b; log K_{ow} = 1.95)
Soil Adsorption K_{oc}:	No experimental sorption data were available. Current Koc estimation methods can not adequately predict Koc values for this type of charged molecule.

Bioconcentration Factor:	< 1.7 (carp fish) (Chem. Inspect. Test Inst., 1992)
Evaporation Rate:	No experimental data are available; however, the very low vapor pressure suggests that evaporation is negligible.
Foliar Half-life (days):	No data were found
Soil Half-life (days):	Insufficient data are available to predict a specific soil half-life. See Water Half-life below for a discussion of biodegradation.
Water Half-life:	Insufficient data are available to predict a specific water half-life. Removal in water will occur through volatilization, abiotic degradation and biodegradation. Volatilization is expected to be negligible. Rhodamine B absorbs UV-light in the environmental spectra above 290 nm (Green, 1990), therefore, it has the potential to directly photolyze in sunlight. In a photolysis study that exposed distilled water solutions of rhodamine B in test tubes to outdoor sunlight, rhodamine B had a mean photodegradation half-life of 61.6 hours (Yager and Yue, 1988); in the environment, this half-life will correspond to direct photolysis at the water surface when exposed to sunlight. Photolysis rates will decrease with water depth as the intensity of light decereases. In addition to direct photolysis, rhodamine B 3 may undergo photo-oxidation in natural water exposed to sunlight. The rhodamine B structure contains functional groups (olefinic bonds, aromatic amine) that are susceptible to photo-oxidants (hydroxyl and peroxy radicals) in natural water (Mill and Mabey, 1985). Based upon the functional groups, half-lives of 1-13 days are possible (these half-lives apply only to conditions of full sunlight at the water's surface). One reported experimental hydroxyl radical constant in water (Buxton, 1988) corresponds to a half-life of about 30 days of sunlight. The BIOWIN computer program (estimates biodegradation from chemical structure) predicts that rhodamine B will have a primary degradation time-frame of "weeks" and an ultimate degradation time-frame of "months" (SRC, 1997).

Air Half-life (days):	0.05 (estimated for gas-phase rhodamine B which will be a very minor component of atmospheric rhodamine B; nearly all will exist in the particulate-phase; method of Meylan & Howard, 1993) Insufficient data are available to predict a particulate-phase half-life. Dry deposition settling rates will depend upon particle size. Since rhodamine B absorbs UV-light in the environmental sprecta (Green, 1990), it has the potential to undergo photolytic degradation; however, kinetic rate data in air are not available.
Plant Uptake Rate:	no data were found
General Information	Basic Violet 10 is classified chemically as a xanthene color. The stearate of this color is Solvent Red 49:1. Use of this color certified as D&C Red No. 19 has been prohibited in cosmetic products in the United States. (CTFA International Cosmetic Ingredient Dictionary, 1991).

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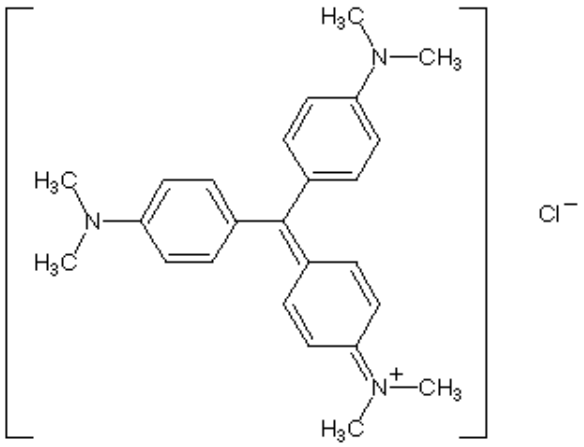
Basic Violet 3



CAS Number:	548-62-9
Molecular weight:	407.99
Melting point (°C):	215°C (dec) (Aldrich, 1996)
Density (g/cm^3):	-----
Vapor Pressure (mm Hg):	< 1 x 10^{-12} mm Hg at 25°C (MPBPVP, 1997)
Water Solubility:	1 g/L at 20-25°C (Baughman et al., 1993) 4 g/L (certified commercial product; Green, 1990)
Henry's law constant:	< 1 x 10^{-14} atm-m^3/mole at 25°C (method of Meylan and Howard, 1991) < 1 x 10^{-14} atm-m^3/mole at 25°C (calculated from vapor pressure & water solubility)
pKa:	-----
Log K_{ow}:	0.96 (Pomona, 1987) 1.16 (Nikaido, 1976) 0.51 (Tsai, 1991)

Note: all log Kow are measured... the preferred value is probably the 0.96 value measured by the Hansch and Leo group at Pomona College.

Dermal Permeability Coefficient:	2.97×10^{-5} cm/hr (estimated by method of USEPA, 1992b; log $K_{ow} = 0.96$)
Soil Adsorption K_{oc}:	No experimental sorption data were available. Current Koc estimation methods can not adequately predict Koc values for this type of charged molecule.
Evaporation Rate:	No experimental data are available; however, the very low vapor pressure suggests that evaporation is negligible.
Foliar Half-life (days):	No data were found.
Soil Half-life (days):	Insufficient data are available to predict a specific soil half-life. See Water Half-life below for a discussion of biodegradation.
Water Half-life:	Insufficient data are available to predict a specific water half-life. Removal in water will occur through volatilization, abiotic degradation and biodegradation. Volatilization is expected to be negligible. Basic violet 3 absorbs UV-light in the environmental spectra above 290 nm (Green, 1990), therefore, it has the potential to directly photolyze in sunlight. However, kinetic data are not available to predict photolysis rates, if any. In addition to direct photolysis, basic violet 3 may undergo photo-oxidation in natural water exposed to sunlight. The basic violet 3 structure contains functional groups (olefinic bonds, aromatic amine) that are susceptible to photo-oxidants (hydroxyl and peroxy radicals) in natural water (Mill and Mabey, 1985). Based upon the functional groups, half-lives of 1-13 days are possible (these half-lives apply only to conditions of full sunlight at the water's surface). It has been reported that basic violet 3 is relatively resistant to biodegradation in the environment and in waste treatment facilities (Bumpus and Brock, 1988). One study found biotransformation rates of 2.4-14.4 days in laboratory batch culture tests (Michaels and Lewis, 1986); however, extrapolation to the environment is uncertain. This study did state that transformation of basic violet 3 was slow compared to many other textile dyes.

	The BIOWIN computer program (estimates biodegradation from chemical structure) predicts that basic violet 3 will have a primary degradation time-frame of "weeks-months" and an ultimate degradation time-frame of "months" (SRC, 1997).
Air Half-life (days):	0.024 (estimated for gas-phase basic violet 3 which will be a very minor component of atmospheric basic violet 3; nearly all will exist in the particulate-phase; method of Meylan & Howard, 1993). Insufficient data are available to predict a particulate-phase half-life. Dry deposition settling rates will depend upon particle size. Since basic violet 3 absorbs UV-light in the environmental sprecta (Green, 1990), it has the potential to undergo photolytic degradation; however, kinetic rate data are not available.
Plant Uptake Rate:	no data were found
General Information	Basic Violet 3 is classed chemically as a triphenylmethane color (CTFA International Cosmetic Ingredient Dictionary, 1991).

Aldrich. 1996. Catalog Handbook of Fine Chemicals 1996-1997. Milwaukee, WI: Aldrich Chemical Co., p. 406.

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Bumpus, J.A. and B.J. Brock. 1988. Biodegradation of crystal violet by the white rot fungus Phanerochaete chrysosporium. Appl. Environ. Microbiol. 54: 1143-50.

CTFA International Cosmetic Ingredient Dictionary. JM Nikitakis, GN McEwen Jr., and JA Wennninger JA, eds. The Cosmetic, Toiletry, and Fragrance Association: Washington, DC (1991).

Green, F.J. 1990. The Sigma-Aldrich Handbook of Stains, Dyes and Indicators. Milwaukee, WI: Aldrich Chemical Co., p.239-40.

Meylan, W.M and P.H. Howard. 1991. Bond contribution method for estimating Henry's law constants. Environ. Toxicol. Chem. 10: 1283-93. [HENRYWIN (v2.61) computer estimation program available from Syracuse Research Corporation]

Meylan, W.M and P.H. Howard. 1993. Computer estimation of the atmospheric gas-phase reaction rate of organic compounds with hydroxyl radicals and ozone. Chemosphere 26: 2293-99. [computer estimation program available from Syracuse Research Corporation]

Michaels, G.B and D.L. Lewis. 1986. Microbial transformation rates of azo and triphenylmethane dyes. Environ. Toxicol. Chem. 5: 161-6.

Mill, T. and W. Mabey. 1985. Photochemical transformations. In: Environmental Exposure from Chemicals. Volume 1. W.B. Neely and G.E Blau, editors. Boca Raton, FL: CRC Press, p.209.

MPBPVP. 1997. Melting Point, Boiling Point, Vapor Pressure Computer Estimation Program (v1.25). Syracuse Research Corp, Environmental Science Center, Syracuse, NY 13210.

Nikaido, H. 1976. Outer membrane of Salmonella Typhimurium transmembrane diffusion of some hydrophobic substances. Biochim. Biophys. Acta, 433:118-132.

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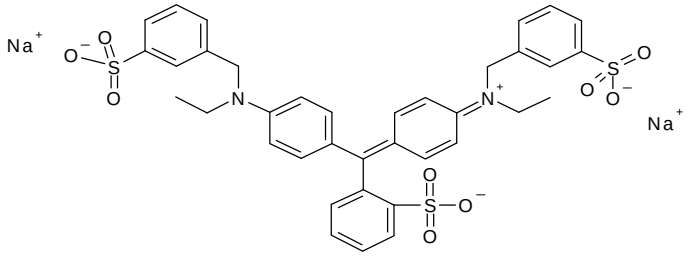
SRC. 1997. Biodegradation Probability Program. BIOWIN v3.61. Syracuse Research Corporation, Environmental Science Center, Syracuse, NY 13210.

Tsai, R.S., N. El Tayar and B. Testa. 1991. Toroidal coil centrifugal partition chromatography, a method for measuring partition coefficients", J. Chromatogr., 538: 119-123 (1991).

U.S. EPA. 1992b. Dermal Exposure Assessment: Principles and Applications. EPA/600/8-91/011B. Interim Report. Washington, DC: US Environmental Protection Agency, Exposure Assessment Group (OHEA).



Acid Blue 9
(disodium salt)

CAS Number:	3844-45-9
Molecular weight:	792.86
Melting point (°C):	283°C (dec) (Aldrich, 1996)
Density (g/cm^3):	-----
Vapor Pressure (mm Hg):	< 1 x 10^{-14} mm Hg at 25°C (MPBPVP, 1997)
Water Solubility:	30 mg/ml (Green, 1990)
Henry's law constant:	<1 x 10^{-15} atm-m^3/mole at 25°C (calculated from vapor pressure & water solubility)
pKa:	-----
Log K_{ow}:	-0.32 (estimated using KOWWIN, 1995)
Dermal Permeability Coefficient:	1.59 x 10^{-8} cm/hr(estimated by method of USEPA, 1992b; log K_{ow} = -0.32)
Soil Adsorption K_{oc}:	No experimental sorption data were available. Current Koc estimation methods can not adequately predict Koc values for this type of charged molecule.
Bioconcentration Factor:	3.162 (estimated using BCFWIN, 1997)

Evaporation Rate:	No experimental data are available; however, the very low vapor pressure suggests that evaporation is negligible.
Foliar Half-life (days):	No data were found
Soil Half-life (days):	Insufficient data are available to predict a specific soil half-life. See Water Half-life below for a discussion of biodegradation.
Water Half-life:	Insufficient data are available to predict a specific water half-life. Removal in water will occur through volatilization, abiotic degradation and biodegradation. Volatilization is expected to be negligible. Acid blue 9 absorbs UV-light in the environmental spectra above 290 nm (Green, 1990), therefore, it has the potential to directly photolyze in sunlight. However, kinetic data are not available to predict photolysis rates, if any. In addition to direct photolysis, acid blue 9 may undergo photo-oxidation in natural water exposed to sunlight. The acid blue 9 structure contains functional groups (olefinic bonds, aromatic amine) that are susceptible to photo-oxidants (hydroxyl and peroxy radicals) in natural water (Mill and Mabey, 1985). Based upon the functional groups, half-lives of 1-13 days are possible (these half-lives apply only to conditions of full sunlight at the water's surface). One reported experimental hydroxyl radical constant in water (Anbar and Neta, 1967) corresponds to a half-life of about 230 days of sunlight. Activated sludge and chemical precipitation treatment of wastewater containing anionic acid dyes resulted in dye removal efficiencies of < 25% for acid blue 9 (FD&C Blue No. 1). Although physiochemical processes showed a variable removal efficiency, they were considered more suitable than the activated-sludge process in the removal of dyes from waste-water (Leal et al, 1986). The BIOWIN computer program (estimates biodegradation from chemical structure) predicts that acid blue 9 will have a primary degradation time-frame of "months" and an ultimate degradation time-frame of "recalcitrant"; in other words, acid blue 9 does not biodegrade fast (SRC, 1997).

Air Half-life (days):	0.07 (estimated for gas-phase rhodamine B which will be a very minor component of atmospheric rhodamine B; nearly all will exist in the particulate-phase; method of Meylan & Howard, 1993) Insufficient data are available to predict a particulate-phase half-life. Dry deposition settling rates will depend upon particle size. Since rhodamine B absorbs UV-light in the environmental spectra (Green, 1990), it has the potential to undergo photolytic degradation; however, kinetic rate data in air are not available.
Plant Uptake Rate:	no data were found
General Information	Acid Blue 9 is classed chemically as a triphenylmethane color. The CTFA Adopted name for certified batches of this color is FD&C blue No. 1. (CTFA International Cosmetic Ingredient Dictionary, 1991).

Aldrich. 1996. Catalog Handbook of Fine Chemicals 1996-1997. Milwaukee, WI: Aldrich Chemical Co., p. 1299.

Anbar,M and Neta,P; 1967. Int J of Appl Radiation and Isotopes 18: 493-523.

BCFWIN. 1997. Meylan W.M. et al. Improved Method for Estimating Bioconcentration Factor (BCF) from Octanol-Water Partition Coefficient. [BCFWIN (v2.0) computer estimation program available from Syracuse Research Corporation].

CTFA International Cosmetic Ingredient Dictionary. JM Nikitakis, GN McEwen Jr., and JA Wennninger JA, eds. The Cosmetic, Toiletry, and Fragrance Association: Washington, DC (1991).

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Leal J.S. et al; 1986. Aqeic Bol Tec 37: 81-89 .

Meylan, W.M and P.H. Howard. 1993. Computer estimation of the atmospheric gas-phase reaction rate of organic compounds with hydroxyl radicals and ozone. Chemosphere 26: 2293-99. [AOPWIN (v1.85) computer estimation program available from Syracuse Research Corporation].

Mill, T. and W. Mabey. 1985. Photochemical transformations. In: Environmental Exposure from Chemicals. Volume 1. W.B. Neely and G.E Blau, editors. Boca Raton, FL: CRC Press, p.209.

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Appendix 2
Product Labels and Material Safety Datasheets

Contents: